

EXTRUSION AND RHEOLOGICAL CHARACTERIZATION OF
CEMENT-BASED MATERIALS CONTAINING DIFFERENT TYPES
OF CLAYS

A Thesis

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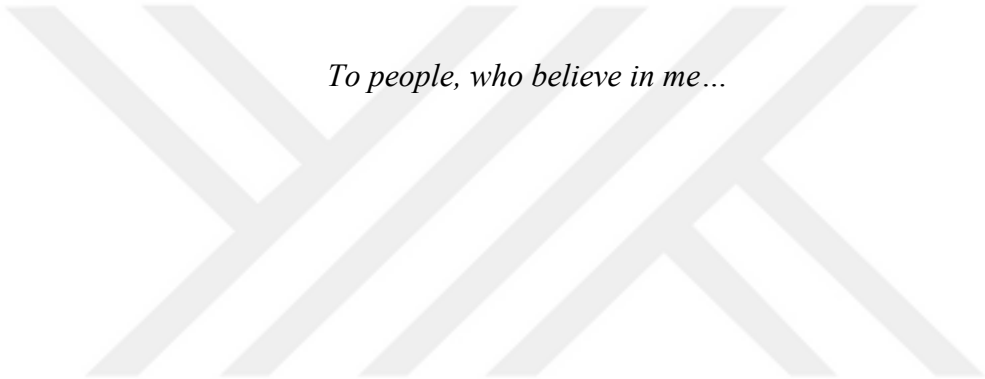
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To people, who believe in me...

ABSTRACT

Recently, digital manufacturing has been termed the fourth industrial revolution (Industry 4.0). Implementation of digital manufacturing revolutionizes the construction industry with the potential of freeform architecture, less raw material consumption, reduced construction costs, and increased worker safety. Thus, for the last decade methods on digital manufacturing of concrete gained a significant interest compared to conventional concrete. While the studies mainly focus on the development of specially designed 3-D printers, at this current technology readiness level the main challenge is to design the highly thixotropic material and the software enabling heterogeneous material flow. In terms of material design, the printable mortars must be extrudable through a nozzle without clogging and retain its shape right after the printing and when another layer is deposited, in short, it must be buildable. To be able to provide layer deposition on top of each other, the consistency of mortar should increase fast upon extrusion. The thixotropic nature of cement paste enables this rapid viscosity change. Time dependent viscosity and shear stress of the material limits the extrusion rate and the height of the construction, fast extrusion rates reduce the buildability, whereas slow extrusion rates create cold joints between the layers and decrease the interlayer bond strength, resulting the overall strength to decrease. These properties could be adjusted by using appropriate materials with appropriate mix design.

This study aims to investigate the influence of 2 different clays, nano-montmorillonite and sepiolite, on rheological properties of fly-ash (FA) amended cement-based systems adapted for 3D printing. Herein, the clays were incorporated at 0.5 and 1% of the cement content. The effects of these clays on rheological properties such as static and dynamic yield stress, apparent viscosity and thixotropy were analysed. The performance of clays was compared to a commercially available viscosity modifying agents (VMA). Finally, selected mixes were printed through extrusion. The results showed that both clays were compatible with

polycarboxylate ether based (PCE) superplasticizer and FA. In fact, the impact of clays on rheological properties were much more pronounced in samples containing 20% FA by weight of cement at a dosage of 0.5% of the cement weight.



ÖZET

Dördüncü endüstri devrimi (Endüstri 4.0) ile dijital üretim önem kazandı. Dijital üretimin uygulanması mimaride tasarım esnekliği, daha az hammadde kullanımı, inşaat harcamalarında azalma ve işçi güvenliğinde artış nedenleriyle devrim yarattı. Bundan dolayı son on yılda betonun dijital üretimi geleneksel betona göre daha çok ilgi görmeye başladı. Çalışmalar daha çok 3 boyutlu (3B) yazıcılara odaklanırken mevcut teknoloji yüksek tiksotropiye ve heterojen malzemelerin akmasını sağlayan yazılımlara yönelmiştir. Malzeme tasarımı konusunda basılabilir harçların nozülde tıkanmadan çıkabilmesi ve basıldıktan hemen sonra ve üzerine başka bir katman geldiğinde kendi şeklini koruyabilmesi, yani inşa edilebilir olması gerekmektedir. Katların birbirleri üzerine basılabilmesi için harcın kıvamının hızlı bir şekilde artması gerekmektedir. Çimento pastasının tiksotropik doğası bu hızlı viskozite değişimine olanak sağlamaktadır. Malzemelerin zamana bağlı viskozite ve kayma gerilmesi ekstrüzyon hızını ve inşa yüksekliğini kısıtlıyor; hızlı ekstrüzyon oranı inşa edilebilirliği düşürürken yavaş ekstrüzyon oranı katmanlar arası soğuk bağlantılara ve katmanlar arası bağ gücünün düşmesine, dolayısıyla da genel olarak mukavemetin azalmasına yol açıyor. Bu özellikler uygun malzemelerin uygun bir karışım tasarımı ile ayarlanabilmektedir.

Bu çalışmanın amacı 3B basım için bir kısmı uçucu kül ile değiştirilmiş çimento esaslı malzemelerde 2 farklı kilin, nanomontmorillonit ve sepiyolit, reolojik özelliklerine olan etkilerini araştırmaktır. Killer %0,5 ve %1 oranlarında çimento ile değiştirilmiştir. Killerin reolojik özelliklerine, yani statik ve dinamik akma gerilmelerine, anlık viskozitelerine ve tiksotropilerine olan etkileri analiz edilmiştir. Killerin performansı piyasada satılan viskozite düzenleyici katkı (VDK) ile kıyaslanmıştır. Son olarak seçilecek karışımlar ekstrüzyon ile basılmıştır. Sonuçlar her iki kilin de polikarboksilat eter bazlı süperakışkanlaştırıcı ve uçucu kül ile birlikte çalışabildiğini göstermiştir. Killerin reolojik özellikler üzerindeki etkisi çimento

ağılıgının %0,5'i kil, %20'si uçucu kül olan numunelerde daha bariz etkileri olduđu görülmüştür.



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Chapter I

Introduction

1.1 General

Concrete is the most used construction material that has many advantages (high compressive strength, castable, readily available in the markets, water resistant, fire resistant, etc.) with relatively a low cost when we consider the large volume constructions [6]. Three-dimensional (3D) printing of the cement-based materials has become a challenge in the construction materials within the 21st century. Additive manufacturing construction is a 3D printing technique that gained huge importance with the 4th industrial revolution, which enabled integration of the digitally controlled systems to the construction.

There are currently available companies, that have started 3D printing of companies, such as WinSun from China, Apis Cor from Russia, Be More 3D in Spain, WASP from Italy, Icon and SQ4D from United States, Constructions 3D and Xtree from France, COBOD from Denmark, Cybe Construction from Netherlands to name a few. Besides the construction companies, architectural firms have also been using the 3D printers to obtain the specific texture on the buildings and to manufacture modular elements by cement-based systems by taking advantage of freedom in the design in 3D printing. According to the Global 3D Concrete Printing Market Information Report, the highest market share with 35,63% belongs to US and the second highest share belongs to Europe by 29,4% on 3D printing market [7]. It has spread all over the world and the main reason for this spread is that it enabled freeform design with complex geometries

[8], the labour needs have decreased, and the cost effectiveness. The cost effectiveness of the 3D printing has been studied by various researchers [9]–[12] and found that the cost effectiveness at complex shape geometries is significantly higher when digital construction methods are used [11].

3D printing parameters are evaluated by two main categories: instrumental parameters and the mix design parameters. The instrument parameters could be named as nozzle geometry, vane system, printing speed, height of the layer, applied force, and software (printing geometry) [13], [14]. The mix design parameters are extrudability, interlayer bonding, printability, and buildability of the cement-based mix [15], [16]. Extrudability is the ability of the mixture to flow through the nozzle, buildability is the ability of the mixture to retain its shape on and the ability of the mixture is to carry the subsequent layers after extrusion, interlayer bonding is the ability of the mixture to bond with the subsequent layers without cold joints and the printability is basically the capacity for a material to be successfully processed via the 3D printing process combining all the above-mentioned criteria [17]–[19].

Conventional concrete mixes consist of cement, water, admixtures, fine and coarse aggregates; however, a printable concrete does not contain coarse aggregates. Aggregates with sizes greater than 2 mm (coarse aggregates) cause clogging at the nozzle and the sand to binder ratio of 3:2 is found to be more effective by providing better resolution by improving the surface finish [20]. Higher ratios of the sand prevent from extrudability by increasing the shear rate. From conventional concrete perspective, only mortars are considered as printable concrete. Even though printable concrete does not contain coarse aggregates, they are still called “concrete”. Admixtures play an important role on printable concrete. Superplasticizers, viscosity modifying agents (VMAs), accelerators and retarders are commonly used admixture types for printable concrete. Superplasticizers enable flow to the system, which is needed for extrudability. There are different types of superplasticizers used in printable concrete: Naphthalene Sulfonate

Formaldehyde (NSF) and Polycarboxylate Ether based (PCE). The difference of these both superplasticizers is the way of adsorption. NSF shows a single-layer adsorption, whereas PCE based superplasticizers show multi-layered adsorption [21]. Most used superplasticizer is the PCE based superplasticizer. The reason is, that the PCE based superplasticizers prevent from flocculation and enables dispersion of the particles [22]. Accelerator and retarders are used for specific applications, meaning that the size of the printing must be considered for the accelerator and retarder dosages to prevent from cold joints (fast setting) [14].

The superplasticizers enable flow, by not promising the mixture to be stable. Most of the time, the amount of the superplasticizers cause segregation. To prevent the mixture from segregation, VMAs is used for holding the free water inside the mixture and they increase the viscosity, which results in thickening. The thickening effect of the mixture prevents it from segregation and provides stability [23]. For printable concrete, the VMAs have been very important due to their stabilities and static natures at rest, but flowable (in traditional concrete) and extrudable (in printable concrete) when the shear force is applied [24]. Generally, VMAs is produced from the modification of high molecular weight polymers. These types of polymers are known to have high steric hindrance and high affinity to water [25]. There are also inorganic VMAs, such as colloidal silica. The negative charges of the inorganic materials interact with the electron deficient calcium of the cement; thus, the gel-like structure occurs. There are also some natural and bio-based VMA's available [24], [26].

Even though VMA usage became a must in printable materials, a printer targeted multi-modelled rheology study was never conducted by any researchers.

It is well known that thixotropy is one of the important properties in all 3D printing applications and neat cement-paste has an inherent excellent thixotropy property due to flocculation. However, 3D printing requires properties beyond the natural thixotropic behaviour of conventional cement-based systems. Most of these rheological parameters are obtained by

keeping the binder to sand ratio lower than conventional mortar mixes. Moreover, the cement content in mortar designed for 3D printing is approximately 25 % higher than conventional mortar mixes. For the last decades, there has been a series of EU initiatives on reducing cement content in concrete to decrease the CO₂ emission from cement manufacturing. Thus, it is required to develop alternative binder blends for 3D printing mortar mixes which contains pozzolans. However, use of any other cementitious material will reduce the thixotropic nature of the cement-based system. Thus, it is crucial to develop more sustainable mixes for 3D printing with improved rheological properties.

1.2 Goal and Objectives

This study aims to investigate the influence of 2 different clays, nano-montmorillonite and sepiolite, on rheological properties of a fly-ash (FA) amended cement-based system adapted for 3D printing. To achieve this goal the impact of clays was evaluated through 3 different rheological shear rate input models: increasing shear rate model, static shear rate model and apparent viscosity model. To understand the influence of size and microstructure, 2 different types of clays, nano montmorillonite and sepiolite, having different particles sizes were used. The outcomes of this thesis will provide an in-depth understanding on how clays “SIMULATE” the rheological parameters by different shear rate models and comparing it to the real-life printing applications.

The specific objectives of this study are to:

- 1- Analyze the mixtures with different types of clays by using the increasing shear rate model and fitting it to the Herschel and Bulkley (H-B) rheological model to obtain the H-B parameters to understand the shear thinning behaviour of the mixtures with respect to time.

- 2- Calculate the dynamic yield stress, viscosities, and the thixotropy of the cement-based systems containing different types of clays and VMA from increasing shear rate model to understand the extrusion behaviour of the mixtures with respect to time.
- 3- Determine the static yield stress values of mixtures containing different types of clays and VMA to understand the buildability with respect to time.
- 4- Identify the influence of high shear to the structural break-down and recovery for cement-based systems containing clays and VMA
- 5- Correlate the mini cone flow of different types of mixtures that contain different types of clays with the related rheological properties
- 6- Establish an extrusion-based printing example with the selected mixes.

1.3 Outline of the Thesis

First of all, a brief introduction to 3D printable concrete is given at Chapter I; then the literature review on generalized 3D printing process, how other researchers evaluated the printability of the 3D printed concrete, the rheology approach of the researchers for printable concrete and the rheology parameters, and the experimented mixture contents are investigated at Chapter II. The materials and methods part is at Chapter III with detailed information about the mixing procedure, mixture contents, used rheological input models and the analysing methods. At Chapter IV, the results from the rheological parameters are shown and discussed. At Chapter V, the study is concluded.

Chapter II

Literature Review

2.1 3D Printing Process of Concrete

The 3D printing process of concrete has mainly three stages: Printer settings, material settings and the printing [27]. The process starts with the CAD (Computer aided design) model, goes to the CAM (Computer Aided Manufacturing) Software. At the CAD model, the desired structures or components are drawn and at the CAM Software, the printing process is simulated by tool-path generation [1] before the real-life printing starts. The advantage of the CAM software is to simulate the printing to identify the stress concentrated zones for a stable structure and generally finite element methods are used for advanced approaches [28], [29].

Before material selection process, it is important to know the design of the 3D concrete printer. The material properties give the insight of the printing process and thus the materials (material proportions, types, etc.) could be adjusted according to the printers, that make them a complementary system. There are 3 main components of a 3D concrete printer: Concrete tank and pumping mechanism, the nozzle and the motion control system [30]. However, the components of a 3D concrete printer could be different from each other. The differences of the components change the printer type. For instance, the 3D concrete printer could be gantry printer [27], [31], which is mounted on the scaffolds and uses X-Y-Z coordinate systems. The extrusion mechanisms could be different. There could be an Auger screw inside the extrusion

system, which provides additional flow to the mixture [32], or the mixture could be pumped by a pumping system [33]. Generally, the processes of 3D concrete printing define the printing systems. Contour Crafting (CC) process is one of the oldest process defined for concrete printing. This process builds the edges outside and then fills inside if it is needed [34]. This process is widely used by the researchers, such as Khoshnevis et al. [35], Moreira et al. [36], Rauhana et al. [37], etc. D-Shape process is another approach to the concrete printing. In this process, the binder is added on the powder material and as the solidification starts, the new layer is added on the top of the previous layer [38]. This process is found by Enrico Dini, who is an Italian Engineer [39]. There are also other techniques developed, such as printing without the support systems and printing by angle, that developed by Apis-Cor [40], and concrete printing with the reinforcement implementation [41]. No matter which process is used, it is important to evaluate the printed sample; so that the structural integrity, high bonding strength and printing quality is satisfied.

2.2 Printability Evaluation

Printability of the concrete could be investigated through single layer or through multiple layers. Sometimes printability and extrudability are confused with each other; however, printability is the combined behaviour of extrudability, buildability, workability, open time and interlayer adhesion [20]. Extrudability is the flow behaviour of the materials and printability is the uniformity of the materials once extruded. The deformations (shrinkage or uniformity) are studied to understand the printability behaviour. The single layer approach could be used for the uniformity of the layers, printing quality (surface finish) and the self-carrying behaviour (buildability).

There is no standard way of measuring printability. Therefore, researchers have evaluated the extrudability, buildability, workability, open time, and interlayer bonding behaviours. In the

study of Ma et al. [42], the extrudability of mortar with copper tailings are investigated through extruding the mortar from an 8x8 mm (square) nozzle, which is a method proposed by Le et al [20]. This study is investigating 2 properties: filament continuity and stability. The filament continuity is investigated by printing 2000 mm long mortars, that have 8 turns in total (subsections are 250 mm-long), which satisfied the continuity and found that the printing speed and extrusion rate are important parameters in order to achieve the goal. The stability of the mortar is evaluated by extruding the mortar layer by layer, on top of each other. As the layers are printed on the top of each other, it is expected to be stable, and also, is expected to carry the subsequent layers. The ability of the filaments, the printed mortar, is expected to carry the self-load and the load applied from the other layers that lie on top. This phenomenon is called the buildability. Buildability could be measured by two approaches: either by printing layer by layer [14], [43] or simulating it by green strength test, which is a measure of the deformation of a fresh concrete [44], [45]. Buildability by “layer-by-layer” printing is measured by two different ways: by shape retention of a single layer or by shape retention of multiple layers. For single layer approach, the ability of the concrete to carry itself is measured, and for multiple layers approach, the ability of the concrete to carry the load of the subsequent layers are measured [46].

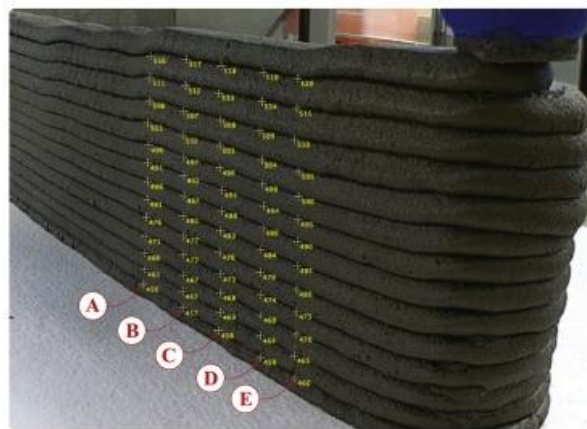


Figure 2.1: Buildability measurement by “layer by layer” printing. The displacements of the extruded concrete are measured [1].

Green strength is a measure of buildability and it is defined as the load carrying capacity of the fresh concrete with little or no deformation, explained by Gibbons et al. [47]. The concrete is placed inside a cylindrical mould and then the mould is removed. In these experiments, the slenderness ratio of the cylindrical mould (h/D ; h = height, D = diameter) of 2 or lower samples are tested to avoid from direct diagonal shear [44]. For instance, in the study of Yuan et al. [2], the slenderness ratio of 1 is used, and the study of Casagrande et al. [48] and Panda et al. [13], the green strength of mortars of different ages and the effect of different sample preparation methods on green strength are investigated. Their results showed that there are 2 possible failure mechanisms, either “barrelling” effect could occur, or crack lines could appear due to shear.

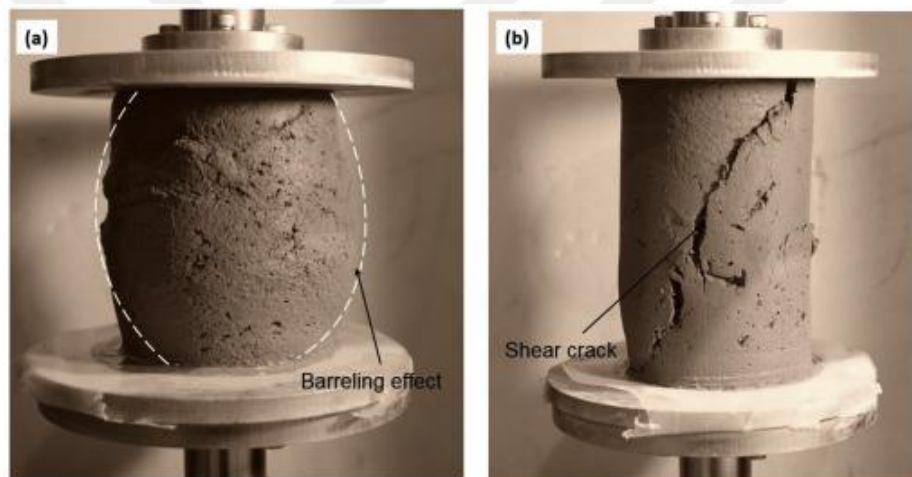


Figure 2.2: Green strength failure mechanism: (a) barrelling effect due to ductile behaviour, (b) shear crack occurring due to increased brittleness [2].

As the buildability of the concrete increases, the workability decreases, however, the workability of the concrete is important to evaluate the open time of the concrete. The open time of concrete could be described as the time interval needed for concrete to remain workable without discontinuities in the extrusion [27]. Unlike extrudability, buildability, workability, and open time; interlayer bond strength is a hardened concrete property. It is a measure of how

strongly the layers are bonded and satisfied the unity. There are several ways to measure the interlayer bond strength. As the weakest strength region is the interfaces of the layers, the stress concentration lowers the strength of the concrete [49]. Splitting test [50] is applied to measure the shear force between the layers by applying the force parallel to the printed layers. Compression tests are also applied [50], [51] to measure the bond strength. Therefore, it enables us to calculate the bonding strength by correlating it to a casted control sample. Pull-out (Tensile-Splitting) tests [50], [51] are applied for direct measurement of the bonding strength. The sample is pulled from two sides that are perpendicular to the printed layers. According to Marchment et al. [52] the surface moisture at the interface must be high for the bonding, and the workability and the interlayer bonding are highly related; therefore, applying cement paste between interlayers increase the bonding ability. Zareian and Khoshnevis [53] reported that, the interlayer bonding is affected by the aggregate sizes, extrusion rate and the thickness of the layers. As these factors increase, the bonding ability also increases.

Even though these parameters are used to evaluate printability, some of the evaluation methods are not standardized and only gives an intuition. Therefore, the fresh properties could be more understandable by their rheologies. The fresh properties of a printable concrete could be measured by cement rheology.

2.3 Rheology of Cement-based Materials

Rheology is the flow behaviour of the materials when they are subjected to forces. Rheology study is important for castability and setting; as the flow behaviour would affect the compaction, voids, and the casting velocity, which are the main parameters for concrete strength and the construction time [54]. There are different types of Rheometers with different types of rheometer configurations, that measure different rheological parameters. Either rotational or oscillatory rheometers could be used for measurement. The rotational rheometers could have

different configurations, such as helical ribbon, anchor, paddle, vane, etc., and different geometries, such as couette, parallel plate or cone; however, the nature of the materials prevent us from measuring the real-time rheology and rheology could only be simulated by assumptions and complex analysis [55].

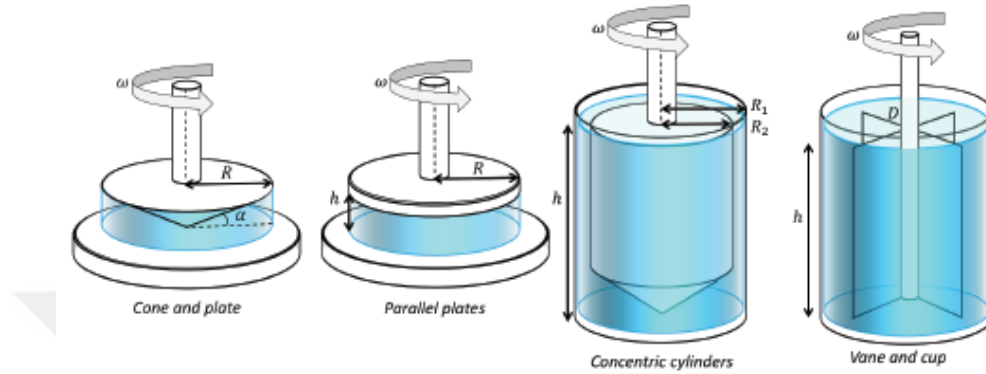


Figure 2.3: Different rotational rheometer geometries: cone and plate, parallel plates, concentric cylinders, vane and cup (left to right) [55]

Oscillatory rheometers could also have different configurations: coaxial cylinders, parallel plates, or vane. These types of rheometers are used for determining the viscoelastic behaviour [56]. As Nehdi & Rahman claimed [57], there are 1 to 2 orders of magnitude difference in the rheological results between coaxial cylinder and vane rotor measurement. The complexities of cement-based materials are due to the reaction of cement with water (hydration mechanism), mixing procedure [58] and time dependency. As the water is introduced to cement, the induction period starts and Calcium-Silicate-Hydrate (C-S-H) gel forms. As a result of this formation, C2S and C3S phases start to nucleate. The increase in the yield stress is due to the hydration products (C2S/C3S) or agglomeration [59].

Depending on the forces between particles, cement paste could either have shear thinning or shear thickening behaviour. According to Roussel, if the van der Waals forces overcome the

hydrodynamic forces, the materials would have shear thinning behaviour at low strain rates; on the other hand, high strain rates would result in shear thickening due to particle inertia [60].

The rheological behaviour of cement-based materials could be analyzed by different rheological models for yield stress and plastic viscosity estimations. The study of Nehdi and Rahman [61] showed that, the different rheological models (Bingham, Modified Bingham, Herschel and Bulkley, Casson, Sisko, and Williamson) could be used for cement-based materials' rheologies by different measuring configurations according to the modelling assumptions. Most used rheological models are Bingham (Equation 1), Modified Bingham (Equation 2), and Herschel and Bulkley (Equation 3) models [62].

$$\tau = \tau_0 + \eta \dot{\gamma} \quad (\text{Equation 1})$$

$$\tau = \tau_0 + \eta \dot{\gamma} + c \dot{\gamma}^2 \quad (\text{Equation 2})$$

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (\text{Equation 3})$$

Where τ_0 is the yield stress, η is the plastic viscosity, c is the fitting constant and K is the consistency of the mixture.

Sometimes Bingham model predictions may result in negative yield stresses, in these cases the use of Herschel and Bulkley model would be a better estimation method, which would yield a higher yield stress, as the model would predict a shear thinning behaviour, or if the cement pastes have a shear thickening behaviour, this model would predict shear thickening behaviour [63]. For modified Bingham model, the power ($n=2$) would predict shear thickening behaviour and a higher yield stress estimation [64] as the assumption is, that the n value of Herschel and Bulkley model would rarely exceed 2, and the fitting in this model would be more accurate [65].

Except from the yield stress and plastic viscosity estimations, thixotropy measurement is one of the fundamental rheological value to be practiced. Thixotropy is known as the structural recovery after the viscosity is gradually decreased by applied shear [66]. Cement is known for its thixotropic nature [67] and measured for various applications. For instance, Assaad et al. [68] aimed to measure and analyse the thixotropy values to investigate the effects of the Self-Compacting Concrete on formwork pressure and found that the increase in the thixotropy resulted in the decrease of hydrostatic pressure applied to the formwork. There are a lot of studies about thixotropy measurement in the literature. Most common approach to measure the measurement is applying flow curve analysis from up and down curves. In the study of Ferron et al. [69], the thixotropy is measured by applying increasing and decreasing flow curves, linear ramp up from 0 s⁻¹ to 300 s⁻¹ and linear ramp down from 300 s⁻¹ to 0 s⁻¹. The area is then calculated between these curves, which is called the hysteresis area.

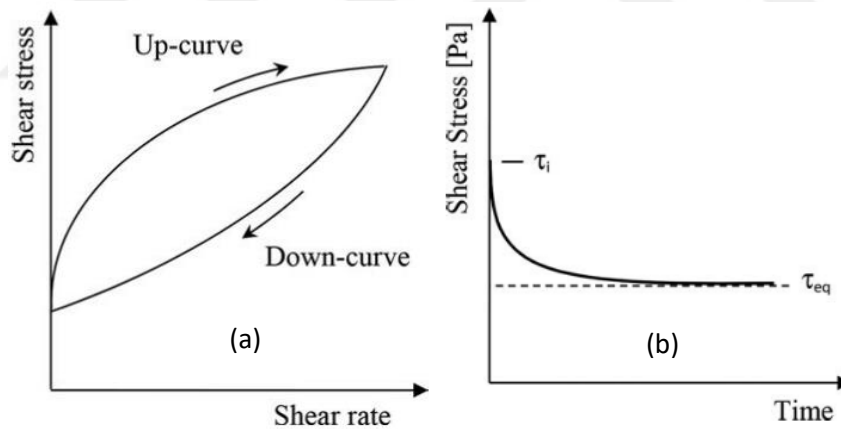


Figure 2.4: (a) A typical hysteresis curve obtained by the flow curve analysis. Hysteresis area is the area between up and down curves. (b) constant shear rate approach for thixotropy measurement [3]

Another approach for thixotropy measurement is the constant shear rate test. In this test, the material is subjected to a constant shear rate, and the shear is applied until the shear stress reached the equilibrium. The initial shear stress is the stress due to the flocculation state, which

is higher than the equilibrium shear stress [3]. There are also other thixotropy measuring techniques, which are conducted without a Rheometer, such as inclined plate test, which was applicable in the field for self-compacting concrete [70]. Thixotropy measurements do not have any standards, however the thixotropic index could be calculated by the slope of the shear stress vs. time plots [71], which was explained in Section 3.3.

2.4 Rheological Properties of Printable Concrete

Rheological properties of a printable concrete are important to understand the flow behaviour of the concrete before it is set. The flow behaviour of the concrete is widely studied by various researchers to correlate the printing requirements (extrudability, buildability, open time, and interlayer bonding) to the rheological parameters.

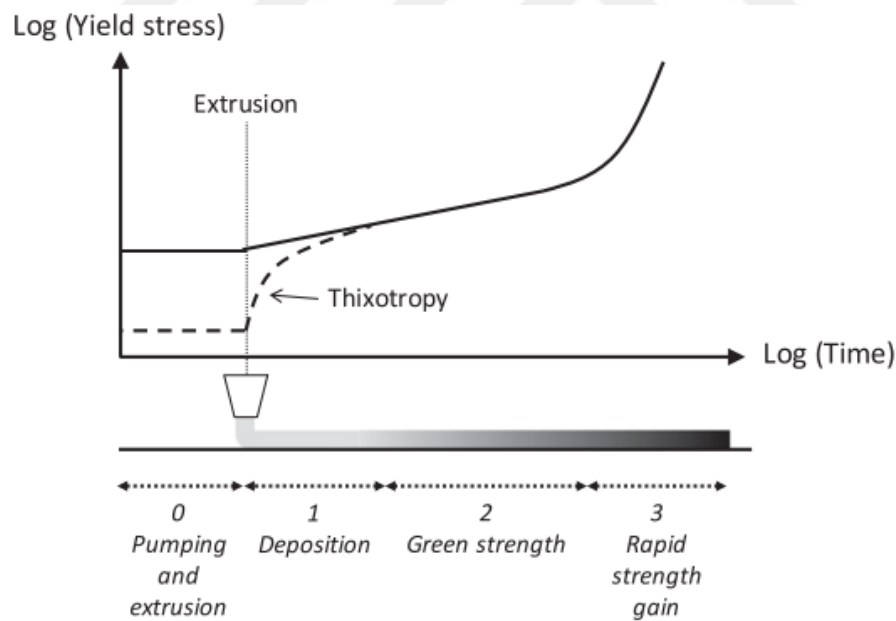


Figure 2.5: Yield stress vs. time relationship of an ideal 3D printable concrete plotted in log scale, showing the correlation of rheological requirements with the printing parameters, by illustrating the extrusion age (darker regions are older) [4].

As shown in Figure 2.5, printable concrete must have low yield stress for extrusion process (and sometimes in pumping process for pumping required concrete printers), increase in the thixotropy at the deposition to remain its shape and prevent from spreading, and increase in the shear stress to carry itself and the subsequent layers. At last, rapid strength gain at later ages is required for the structural stability (for setting) [4], [72].

In terms of yield stress, there are two distinguishable yield stresses: static yield stress and dynamic yield stress. Static yield stress is the minimum stress required to initiate the flow behaviour, whereas dynamic stress is the minimum stress to maintain the initiated flow. In this sense, the dynamic stress is studied for extrudability, and the static yield stress is studied for buildability. In extrusion, the shear force is applied to have continuous flow; after the extrusion, the material is at rest (static) and it needs to carry the self-load and the load applied from subsequent layers [73]. The study of Figueiredo et al. [74] showed that, the extrusion speed is an important parameter, that affected the rheological parameters. In static yield stress measurements for printable concrete, different constant shear rates were applied by various researchers. In the study of Panda et al. (2019) [75], shear rate of 0.5 s^{-1} was applied to measure the static yield stress of 3D printable geopolymers nanocomposites, whereas in another studies of Panda et al. [76], [77], shear rate of 0.1 s^{-1} was used. This shows that the shear rate application is subjective and could be applied at any rate, that is relatively low.

Apart from yield stress measurements, thixotropy measurements of printable composites have become a wide study area for rheological studies. According to Rahul et al. [78], the increase in the yield stress with time is affected by the increase of thixotropy. This phenomenon is important for the materials to be extrudable, but also important to remain their shapes right after they are extruded [77]. According to Panda et al. [76], better shape stability and high buildability depend on high thixotropy. A thixotropic model for 3D printable materials

(Equation 4) is developed by Kruger et al. [79], which combines the thixotropic model of Roussel (Equation 5) [71].

$$\tau_s = \tau_D + R_{thix} \cdot t \quad (\text{Equation 4})$$

$$\tau_s = \tau_{S,i} + A_{thix} \cdot (t - t_{rf}) \quad (\text{Equation 5})$$

Where τ_s is the apparent shear stress, τ_D is the dynamic yield stress $\tau_{S,i}$ is the static yield stress, t is the time, t_{rf} is the time period of re-flocculation, R_{thix} is the Re-flocculation rate and A_{thix} is the structuration rate.

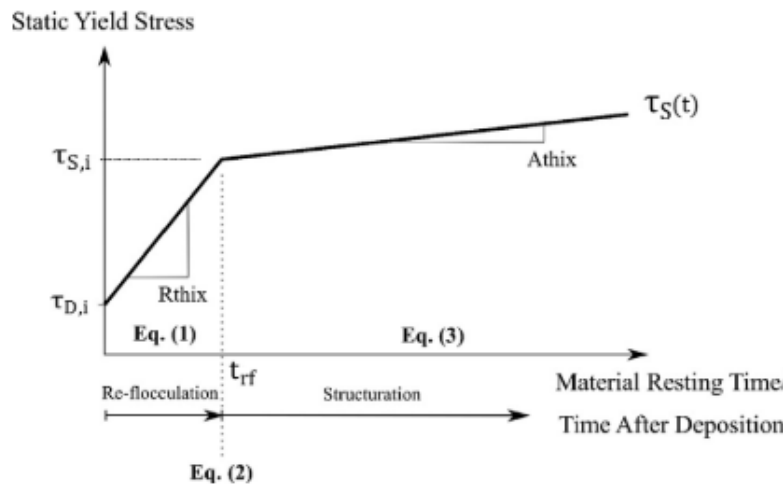


Figure 2.6: Relationship between the R_{thix} and A_{thix} values. Time dependent behaviours in re-flocculation and structuration states are represented [79].

Thixotropic behaviour of the materials enables the material to flow under shear and gain its strength in short times to carry itself and the other layers. An ideal thixotropic material illustration for printable concrete was shown in Figure 2.7 [80]. At that study, the thixotropic behaviour of the materials was not investigated by the hysteresis area, instead, they have measured the workability loss as an index of this type of behaviour.

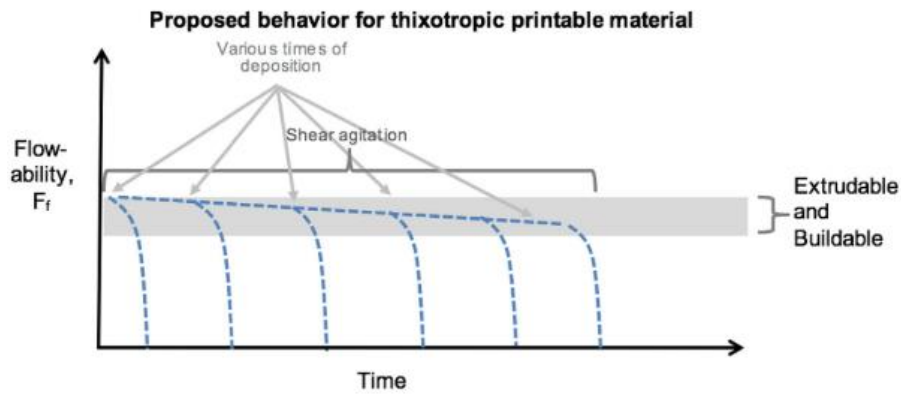


Figure 2.7: Illustration of various deposition times in terms of flowability for a thixotropic printable material proposed by Soltan and Li [78].

Even though cement is a thixotropic material, the researchers have found that the thixotropic behaviour of cement was insufficient, and they have investigated to enhance the thixotropic behaviour by replacing or adding different materials such as VMAs, clays and chemical admixtures.

2.5 Composition of Printable Cement-based Materials

The first requirement to be fulfilled is the flowability of printable cement-based materials. In this sense, the VMAs are used to provide additional flow. The water to binder ratio (w/b) was found crucial for the shape stability [74]. There are different types of superplasticizers studied for printable concrete, such as NSF (Naphthalene Sulphonate Formaldehyde) and PCE (Polycarboxylate Ether). A comparative study was done by Qian and de Schuetter [21], by comparing the differences of NSF and PCE superplasticizers. They have found that the increase in the amounts of SP of both types resulted in decreasing the dynamic stress and the thixotropic index. As NSF has a single layer, and PCE has a multilayer adsorption behaviours, the saturation of NSF by adsorption is much more possible; and for this reason, the responses in the dynamic stresses are different, as the PCE needs to fill other layers fully. Even though NSF

is found to be a better in this study, PCE type of superplasticizers were studied for printable concrete due to their high range water reducing and dispersing properties. In addition, they are found to be the most suitable SPs that work with the clays better [81]. Extrudability of the cement-based materials have converse effects with buildability. To eliminate this contradictory effect, the use of VMAs have been important for their thixotropy enhancing natures. The Hydroxy Propyl Methyl Cellulose type of VMA amount in printable concrete was studied in [82], and it was found that increase in the amount of this type of VMA resulted in increased pressure during extrusion, enhanced the shape stability and improved the consistency of the extruded filament. On the contrary, the VMA usage must be limited. The study of Chen et al. [83] proved that too much of VMA usage resulted in poor compaction and high porosity. The thixotropy of the mixtures could be also increased by using nano-clays (NCs). According to a study of Qian et al. [84], nano-clay addition resulted in the increase of the yield stress by filling and inter-bonding effect. According to van Olphen, as cited in Marchon et al. [4], the oppositely charged surfaces of the clays leads them to behave like a viscosity modifier, that flow under shear and gain immediate strength at rest. The reason behind this behaviour is that the clays have layered structure with alternating octahedral alumina and tetrahedral silica layers. In between those layers, there exist interchangeable ions that attract water [5].

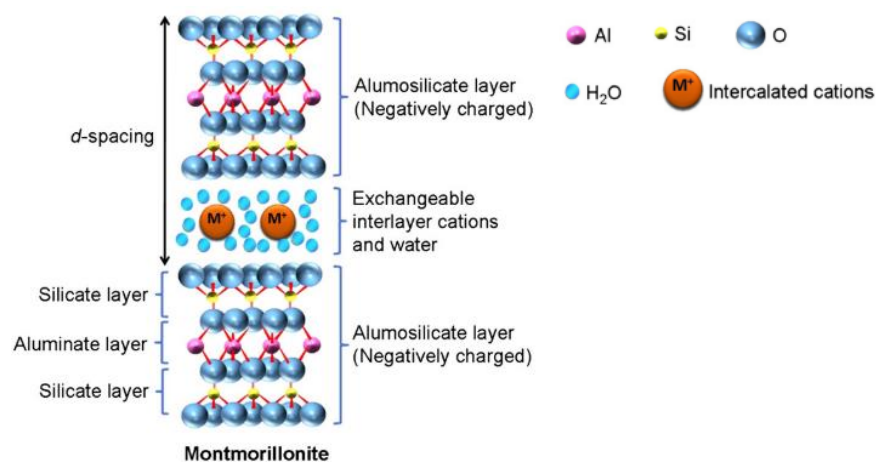


Figure 2.8: Illustration of montmorillonite clay, and the d-spacing of the structure. The Al, Si, O, Interlayer cations and H₂O are shown on the figure [5] .

The effects of the clays have been widely studied by various researchers. As it is shown in Table 2.1, printability properties have been investigated by various mix designs and they found that traditional concrete needs to be modified in a way that satisfies all of the printing requirements.

Table 2.1: Literature summary of printable cement-based mix design and compositions with pozzolan (%weight of cement), water to binder ratio (W/b), sand type with maximum sand size, sand:binder ratio (w/w of cement), SP type and amount (in mL or x/w of cement), VMA type and amount (w/w of cement), additional admixture type and amount (in mL or w/w of cement), fiber types and amount (w/w of cement) and the printability investigation target

Researcher	Pozzolan (w/w of cement)	w/b	sand type & max. sand size (mm)	sand:binder (w/w of cement)	SP (mL (w/w of cement)	VMA	Additional Admixture	Fibers (w/w of cement)	Investigation of Printable properties via:
Jayathilakage et al.[85]	Silica Fume (11%wt.)	0.25	1.18 mm	0.56 (coarse) 1.11 (fine)	0,9 mL	-	Retarder (0,6 mL)	-	Aggregate size and amount
Panda et al.[77]	Fly Ash (70%wt)	0.40- 0.45	Fine River Sand -2 mm	1:3	NA	Nanoclay	Activator (3% wt)	-	VMA effects
Stlavcheva & Artamonova [86]	NA	0.23- 0.25	NA	NA	PCE based - 0.2 %wt.	Xanthan Gum/ Potassium pyrophosphate/Liquid Glass-0.2 %wt.cement	-	-	VMA effects
Jo et al. [27]	NA	0.29- 0.33	0.7 mm & 0.8 mm	2:1-1:1-2:3	NA	-	-	PVA- 0.1, 0.2, 0.3 (%wt.)	Fiber addition Sand amount
Zhang et al. [87]	NA	0.22- 0.26	Natural sand 4.75-2.36-1.18	1.91-1.56- 1.18-0.9	PCE based- 0.8%wt.	Silica Fume Nano-silica Micro-Attapulgate Clay	NA	NA	Aggregate size and amount; VMA effects
Rahul et al. [88]	Class F Fly Ash Silica Fume	262 g	Quartz sand	3:2	PCE based	Micro-Attapulgate Clay(0.3 % w of binder) HPMC based VMA (solid) (0.1% w of binder)	-	PP microfibers	VMA effects
Xiao et al. [89]	NA	0.35	Natural/Recycled - 0.9 mm	1:1	PCE based	Nanoclay	-	-	Recycled aggregate usage

Chapter III

Materials and Methods

3.1 Material Selection and Properties

Cement-based systems were prepared by fly-ash amended cement binders. Cement paste samples were prepared by Akçansa Ordinary Portland Cement (OPC) CEM I 1 42.5 R. OPC was replaced by F type FA (20% w/w). Table 3.1 summarize the chemical composition of FA and OPC used in the study. A Mastersizer 2000 particle size analyzer equipped with a Hydro MU 200 wet dispersion unit (Malvern, Worcestershire, United Kingdom) and a sonicator were used to determine the particle size distribution (PSD) of cement. Figure 3.1 represent the particle size distribution for the FA and OPC used in the study. FA are known for their relatively large particle sizes with respect to cement and for their circular shapes that provide additional flow to the fresh cement pastes [90]. To improve the workability of the cement paste Sika Viscocrete High-Tech is a PCE based superplasticizer was used in the experiments that contains 25-30 wt. % trimethyl stearyl ammonium. These particular type of superplasticizers are known for their thixotropy enhancing behaviour [91].

Table 3.1: Chemical composition of Fly Ash

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	SO₃	Na₂O	K₂O	Others
FA	55,38%	25,50%	6,14%	2,02%	2%	0,14%	0,62%	3,80%	6,40%

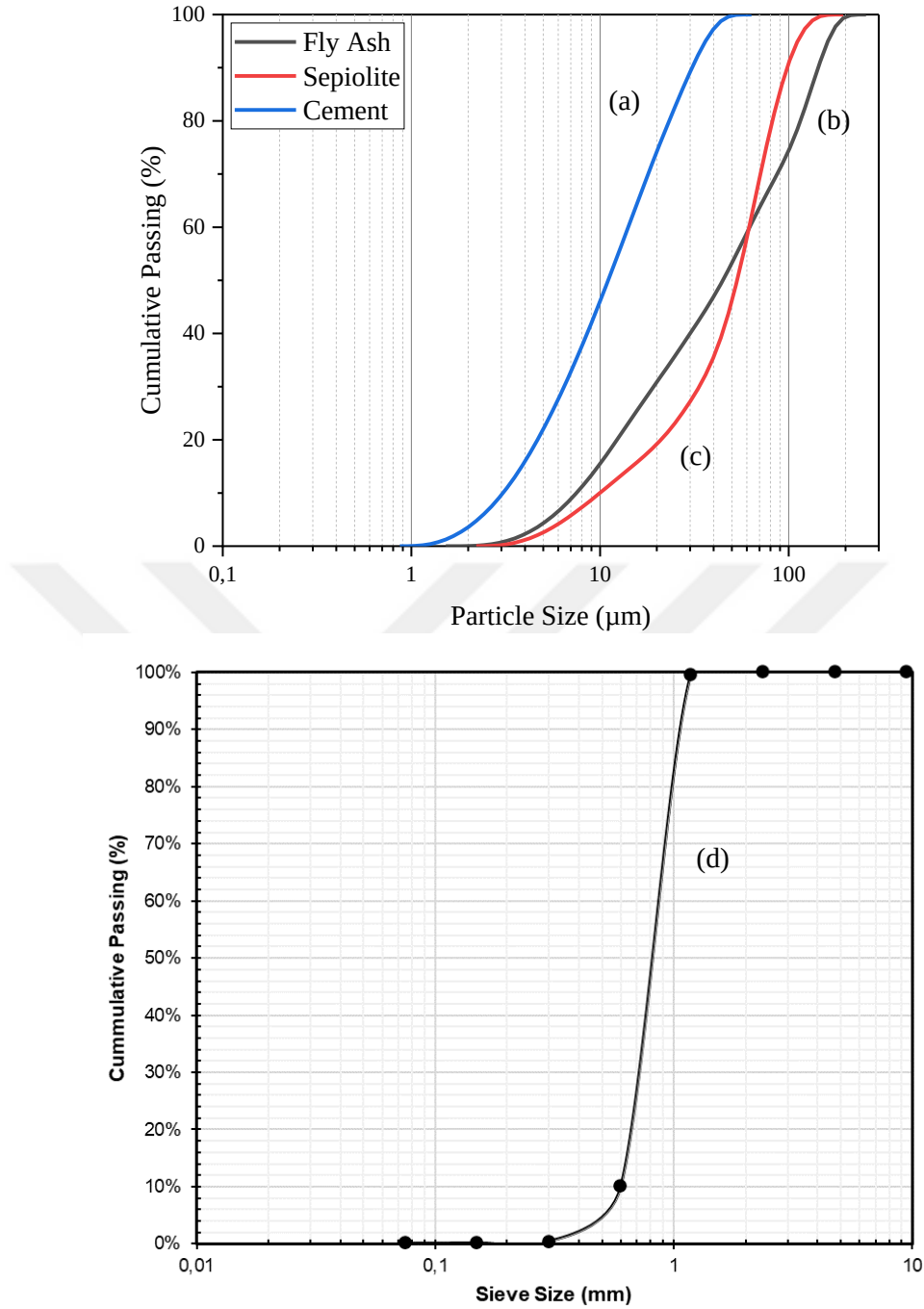


Figure 3.1: Particle sizes of (a) Akçansa CEM I 42,5R, (b) Class F Fly Ash and (c) Sepiolite (d) natural sand given in micro-meters with cumulative passing%.

Besides the binders, 2 different types of clays were used as thixotropic agents: Surface modified Nano-montmorillonite (NM) and Sepiolite. NM is known for its thickening behaviour up to a dosage of 1% and high pozzolanic activity in small amounts. High amount of NM results in

agglomeration and lowers the pozzolanic activity [92]. Sepiolite is known for its needle-like structure that forms gels and viscosity enhancing properties by providing stability to the suspension systems [93]. While NM was obtained from as surface modified from Sigma-Aldrich [94], the sepiolite clay was obtained from a local resource. The average particle size of the cement is 15 μm , fly ash is 65 μm and sepiolite is 57 μm ; and the maximum particles size of NM was reported as 20 μm by Sigma-Aldrich.

3.2 Sample Preparation

Cement paste samples were prepared with the materials listed in Section 3.1. A water to binder (w/b) ratio of 0.36 was used through all the mixtures. The SP content was adjusted to obtain a similar flow diameter in mini slump conte ($\pm 10\%$). Table 3.2 summarizes the mix design of the cement paste samples used in the experimental evaluation.

Table 3.2: Mix design of cement-based systems used in experimental program (wt.%) The w/b is 0.36. (OPC: Ordinary Portland Cement; FA: Fly ash; NM: Nano-montmorillonite; SEP: sepiolite; SP: Superplasticizer, Sika Viscocrete High-Tech; VMA: viscosity modifying agent, Sika Stabilizer 4R-7)

Sample Name	Binder Phase				Additives	
	Cement	Fly Ash	NM	SEP	SP	VMA
control_SP	100	-	-	-	0,35	-
control_SP_FA	80	20	-	-	0,35	-
nm_0.5	99,5	-	0,5	-	0,35	-
nm_0.5_FA	79,5	20	0,5	-	0,35	-
nm_1	99	-	1	-	0,35	-
nm_1_FA	79	20	1	-	0,35	-
sep_0.5	99,5	-	-	0,5	0,5	-
sep_0.5_FA	79,5	20	-	0,5	0,5	-
sep_1	99	-	-	1	0,5	-
sep_1_FA	79	20	-	1	0,5	-
vma_SP	100	-	-	-	0,5	0,3
vma_SP_FA	80	20	-	-	0,5	0,3

Cement paste samples were prepared by ASTM C305-14 Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars [95]. To provide homogeneity in the mix, the

standard mixing procedure was modified. Such as, the mixing water and SP were first mixed separately at 1000 rpm for 1 minute prior to the mixing and then added to the dry blended binder. Then, the waiting period was extended to 75 seconds rather than 15s as mentioned in the standard. The mixture was scraped for 30 seconds and waited for additional 45 seconds to enable the cement to absorb the water fully. Then, the final mixing stage was done for 2 minutes in high rpm instead of 60s. In addition, for the samples containing clays, clays were also added into the mixing water and SP suspension and mixed at 1000 rpm for 1 minute. For the mixtures with VMA, the mixing water is divided into 2 portions with ratio of 1:4. One fourth of the water was mixed with VMA and the remaining 3/4th was mixed with SP. The SP and water solution was again mixed at 1000 rpm and then directly added to the dry binder at the beginning of the mix. However, VMA/water solution was mixed the final mixing stage after the 75 seconds of resting.

3.3 Rheological Analysis

Rheological experiments were conducted by Anton Paar rotational rheometer Rheolab QC with the vane and container geometry. The volume of the cement pastes was kept constant at 40 mL for more precise measuring. To evaluate the rheological properties, 3 different shear-rate controlled rheological models were used.

3.3.1 Increasing Shear Rate

A pre-shear stage was applied prior to the testing where the shear rate was kept constant at 300 s⁻¹ for 60s. Pre-shear was done to eliminate the mixing history of the mixture due to the agglomerates [96]. Upon, pre-shear the sample was let at resting for 5 minutes, to enable the stabilization of the mixture after mixing it at high shear rates. Then, the shear rate was increased

to 100 s^{-1} from 0 s^{-1} in 60s (up-curve) and then, decreased back to 0 s^{-1} from 100 s^{-1} in 60s (down-curve). To evaluate time-dependent behaviour of cement-paste, the samples were re-tested by the same shear profile without pre-shear stage after 10 min of waiting and the change in rheological parameters was recorded. The first measurement after the pre-shear was considered as $t=0$, and it was followed by $t=10, 20$, and 30 min . Figure 3.2 summarizes the shear rate profile used in the evaluation.

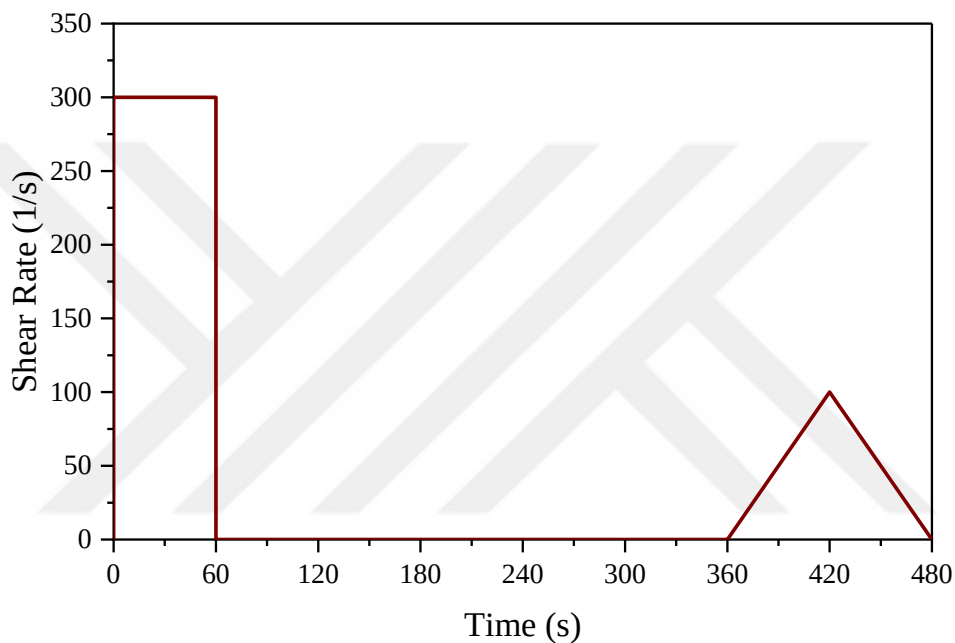


Figure 3.2: Increasing Shear Rate input: 1 min. preshear @ 300 s^{-1} , 5 min. wait, increasing shear rate $0-100 \text{ s}^{-1}$ in 60 seconds, decreasing shear rate $100-0 \text{ s}^{-1}$ in 60 seconds, and then kept at rest for 10 min. (1st loop). The up and down curve loops were repeated for 4 times in total. As the first measurement after pre-shear was considered as $t=0$, and then followed by $t=10, 20$, and 30 min

This model provides us the information about the dynamic yield stress, viscosity, and the hysteresis area. The dynamic yield stress is found by the Herschel and Bulkley (H-B) model (Equation 3) (See Section 2.3), which is used for identifying the degree of the shear thinning/thickening behaviour. The analysis conducted by using the down-curve obtained at each interval.

Equation 3 describes the H-B model, where τ_0 is the yield stress (Pa), K is the consistency index (Pa.s), and $\dot{\gamma}$ is the shear rate (s^{-1}). Herein, “ n ” is parameter indicating the flow index of the material. If $n < 1$, then the material demonstrates a shear-thinning behaviour with increasing shear, whereas the material exhibits shear-thickening behaviour when n is larger than 1. The dynamic yield stress and plastic viscosity of the samples were calculated by using the down curves obtained at various time intervals.

Thixotropy could be described as the property of complex fluids becoming thinner when constant shear rate is applied and be able to recover its viscosity fully to the initial state in an appropriate period of time after the load is removed [97]. A simple method to evaluate the thixotropic nature of the material is to analyse the hysteresis area between the up-curve and down-curve. Thus, to quantify the thixotropy of the samples areas between two curves were calculated for each testing interval. All analyses were done on triplicates of cement-paste samples.

3.3.2 Static Yield Stress

Static yield stress model describes the yield stress evolution of the mixture with respect to time and for the printing process, it evaluates the yield stress of a printed layer to understand the static ability of the mixture. After a layer is printed, it is important for it to be stable after printing, in other words, it needs to remain its shape and buildable as more layers are printed on the top of each other [85].

As shown on Figure 3.3, a pre-shear stage was applied at $300s^{-1}$ at 60s prior to the testing to provide homogeneity. After 5 minutes of waiting, the mixture is mixed at a relatively low constant shear rate of $0.1 s^{-1}$ for 1 minute, which is an almost non-deforming shear rate. To evaluate time-dependent evolution of the static yield stress, the samples were re-tested by the

same shear profile without pre-shear stage after 5-minutes. The first measurement is considered as $t=0$, and it was followed by $t=5, 10, 15, 20, 25$ and 30 min (See Figure 3.3). All analyses were done on triplicates of cement-paste samples.

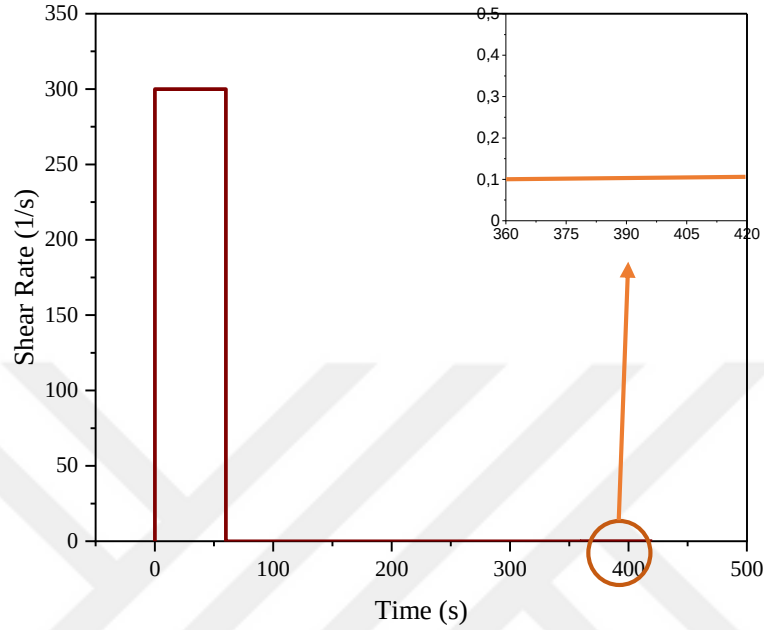


Figure 3.3: Static yield stress shear rate input with respect to time: 1 min. preshear @300 s-1, 5 min. wait, 1 min. constant shear at 0,1 s-1 (1st loop). Loops were repeated without the pre-shear interval for 6 times.

Additional evaluation on thixotropy was done by calculating the time dependent change in static yield stress. The structural build-up at small shear rates has become more important than the structural breakdowns at high shear rates [97]. The structural build-up of cement paste samples were quantified by A_{thix} index calculations. This was found to be a more accurate approach to measure thixotropy compared to hysteresis as a method by indicating structuration (Structuration rate) of cement paste [73]. A_{thix} index was calculated by the slope of the curve obtained by yield stresses at different time intervals (every 5 minutes) [96] (Equation 6).

$$A_{thix} = \frac{\tau_{0,f} - \tau_{0,i}}{t_{0,f} - t_{0,i}} \quad (\text{Equation 6})$$

3.3.3 Apparent Viscosity

As mentioned before, thixotropic nature of cement-based materials is related to shear-thinning nature of the material. It is a time-dependent behaviour of the material, such that the viscosity of the material must recover after a certain period of time when the applied shear rate is removed. A simple approach to evaluate the structural breakdown/recovery upon loading and unloading is a “step model”. The step test consists of 3 intervals at 2 different constant shear rates. The first and last intervals are performed at a low shear rate of 0.1 s^{-1} for 60 s and the second interval is performed at a high shear rate of 300 s^{-1} for 60 s (Figure 3.4). All analyses were done on triplicates of cement-paste samples.

This model would provide the insight about the material during and after the extrusion. The recovery percentage tells us the ability of the paste to recovery in viscosity after the structural breakdown [77]. If the viscosity loss of the mixtures is low, this means that the mixture was able to build up its strength.

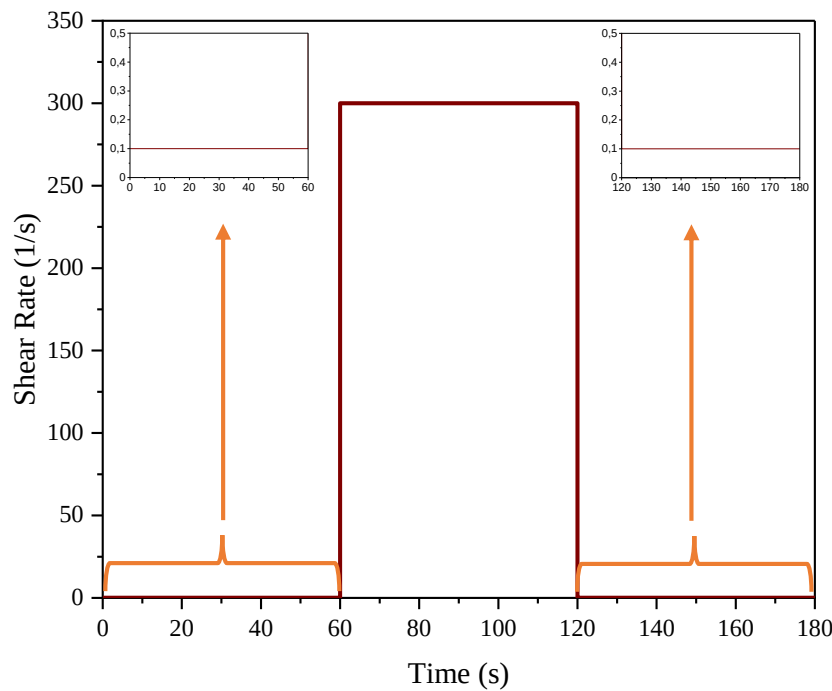


Figure 3.4: Apparent viscosity shear rate input with respect to time. 1 min. preshear @ 300s^{-1} , 1-minute constant shear @ 0.1 s^{-1} , 1-minute constant shear @ 300s^{-1} and 1-minute constant shear at 0.1s^{-1} .

3.3.4 Mini Slump Cone

The rheological analyses are supported by the mini slump cone tests by measuring the 2D flow diameters of the cement pastes, as the mini cone test has a strong relationship with the yield stress of cement pastes [98]. The mini cone shown in the Figure 3.5 is put on a clean plexiglass, filled fully with the cement paste and the height of it is evened out. The cone is drawn away fast and waited until the flow of the cement paste has stopped. 4 diameters at even angles are measured at $t=0,15,30,45,60$ minutes.

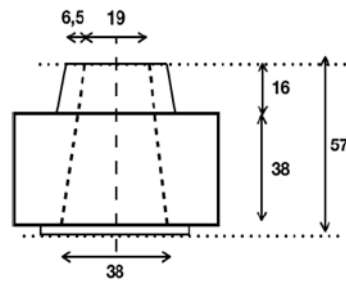


Figure 3.5: Scheme of mini slump cone in mm.

3.3.5 Preliminary Printing Trials

Upon completion of rheological analyses, 3 different cement-based systems were selected for preliminary printing. The printing evaluations are done by mortar samples by simply incorporating sand with particle size between 0.5-1 mm. While the w/b ratio and all mixing components of cement paste were kept constant, the binder to sand ratio was kept at 1:1.5.

The preliminary printing trials were carried out by a ram extruder attached to a robotic arm (see Figure 3.6). The printing speed was determined to be approximately 15 mm/s and the thickness of the layers were set to 15 mm. A square nozzle geometry was used for printing.

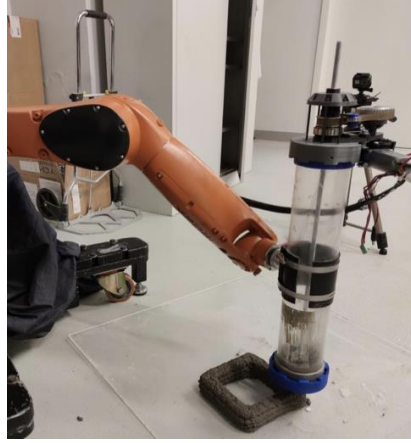


Figure 3.6: Lab scale extruder used for preliminary printing evaluation

Mixing time is taken as $t=0$ at the time the mixing water is introduced to the cement. The mixture is loaded at $t=7$ min and started printing at $t=8$ min. The printing geometry was given as follows in Figure 3.7.

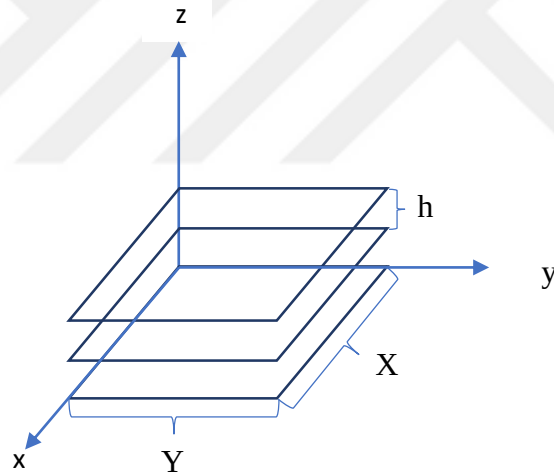


Figure 3.7: Preliminary printing geometry, where $|X|=|Y|=15$ cm and $h=15$ mm

Chapter IV

Results and Discussions

4.1 Intrinsic rheology of cement paste and the influence of commercially available VMAs on rheological performance of cement-based materials

The fresh state for 3D printing concrete requires ease of pumping, proper compacting capabilities while placed at print head whereas without the print head, the material should be able to support itself with an adequate stiffness [9]. These properties of concrete are governed by the composition of the matrix which dominates the yield stress and thixotropic behaviour of the mix. Corresponding improvements on fresh concrete qualities can be obtained by the use of chemical admixtures like superplasticizers, VMA and clay based mineral additives. Thus, the first set of evaluation on rheological behaviour of cement-based systems were conducted on cement paste samples containing PCE superplasticizers and FA. Figure 4.1 presents the shear profile for control neat cement paste samples. The analyses were done on triplicates of samples on each mix and samples belong to the same set of mix showed similar rheological profile. So, one representative graph for each set of mix was shown but the average values and standard deviation in Table 4.1 was calculated from triplicates of samples (See Appendix A for other trials).

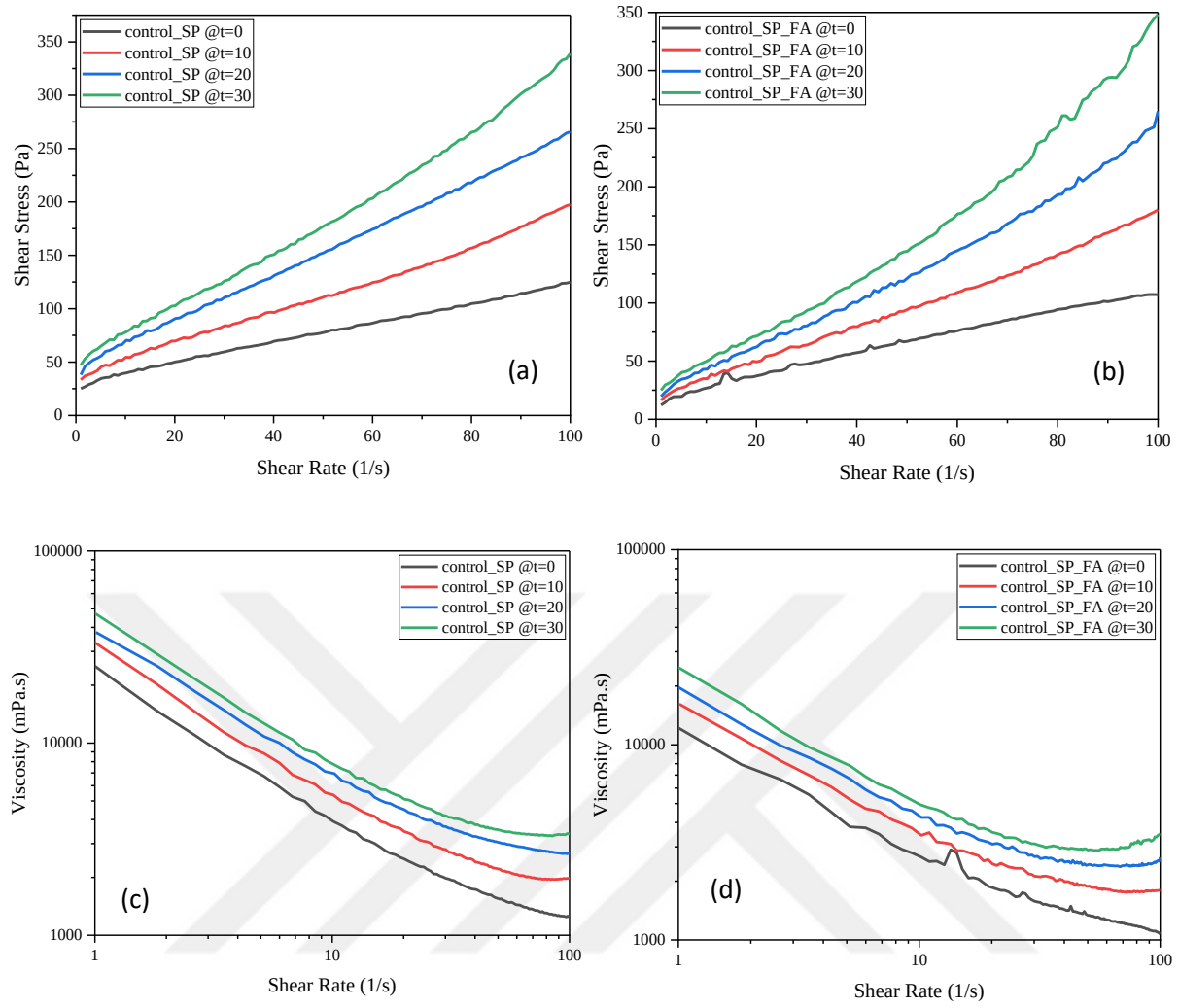


Figure 4.1: Shear and Viscosity Profiles of control samples obtained from the increasing shear rate model. (a) shear profile for Control_SP sample at different time intervals (b) shear profile for Control_SP_FA sample at different time intervals (c) Viscosity profile for Control_SP sample at different time intervals (d) Viscosity profile for Control_SP_FA sample at different time intervals. The profile was analyzed by H-B model using the down-curve of the hysteresis loop. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

As mentioned before the rheological evaluation was done based on H-B model. The presented yield stress results were calculated from the regression line of the downward flow curve. Based on the analyses, the dynamic yield stresses for Control_SP and Control_FA samples were calculated as 26,9 Pa and 11,6 Pa, respectively (see Table 4.1). This was expected with incorporation of fly ash particles would increase the workability due to their spherical particle shape improving the motion of particles during applied shear rate [99]. The time-dependent evolution of the shear profile and the dynamic yield stress would also be an indicator of

structural build-up for the cement paste samples. Incorporation of FA by 20% of cement weight would expected to slow the hardening rate thus it would decrease the rate of structural build up. The relative increase in dynamic yield stress at $t=30$ min to $t=0$ min for Control_SP sample was 31.%,where as it was 23.3% for Control_SP_FA sample. While incorporation of FA decreased the yield stress, it did not affect the consistency index of the mix at $t=0$. Incorporation of FA increased the fine particle content and improved the consistency of the mix. Both samples exhibited shear-thining behaviour. Since incorporation of FA increased the flowability of the mix, there was slight decrease in rate of shear-thinning in Control_SP_FA sample compared to Control_FA (Figure 4.1 c-d) However, the significant decrease in K value for Control_SP_FA sample at $t=20$ and $t=30$ min is an indicator of possible segregation. Thus, it is critical to use additional admixtures or mineral additives such as clays to improve the robustness of the mix.

Table 4.1: The average H-B parameters (K, n and τ_0) and thixotropy values obtained from the area between the up and down curves obtained from increasing shear rate model at $t=0,10,20,30$ for control mixtures.

Sample Name	time (min)	Average				
		K [Pa.s]	n	τ_0 [Pa]	τ_0 [%increase]	Thixotropy [Pa.s]
control_SP	0	1,4	0,9	26,9	0,0%	1183,2
	10	1,1	1,1	38,9	44,6%	1409,8
	20	1,7	1,1	47,7	23,0%	2793,3
	30	1,2	1,2	62,7	31,5%	5552,8
control_SP_FA	0	1,8	0,9	11,6	0,0%	178,3
	10	1,1	1,1	19,7	75,7%	1785,1
	20	0,5	1,3	30,5	57,1%	2940,6
	30	0,3	1,5	37,6	23,3%	3072,7

Then, further analysis was done to evaluate the thixotropy of the samples by calculating the area enclosed between up-curve and down-curve as shown in Figure 4.2 (Only $t=0$ and $t=30$ min are presented in the text, the remaining plots can be found in Appendix B). As expected, incorporation of FA reduced the thixotropic nature of cement-paste.

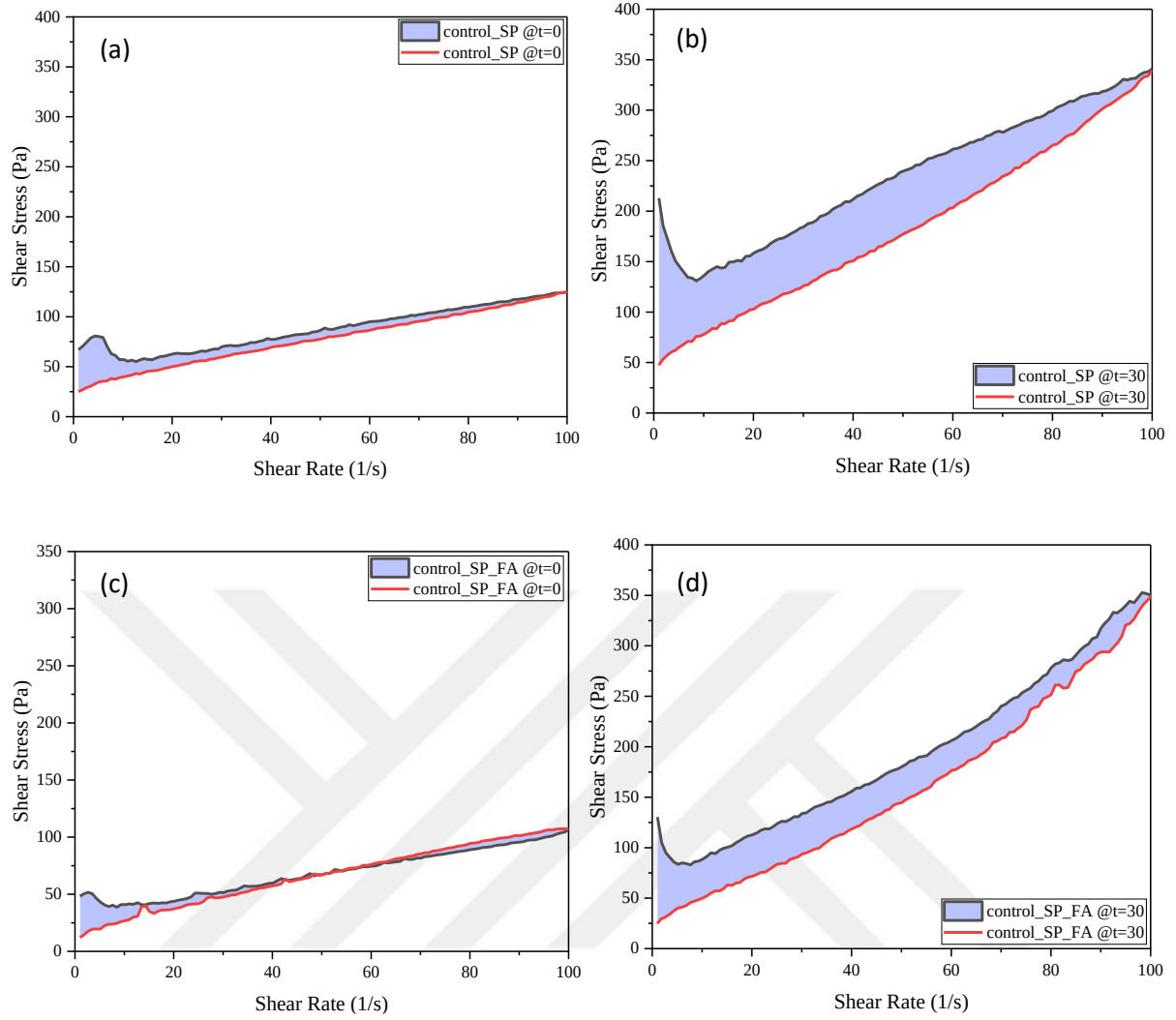


Figure 4.2: Hysteresis areas for Control_SP and Control_SP_FA mixture obtained at $t=0$ and 30 min. The areas are between the up and down curves, shown in blue color. (a) Hysteresis area for Control_SP sample at $t=0$ (b) Hysteresis area for Control_SP sample at $t=30$ (c) Hysteresis area for Control_SP_FA sample at $t=0$ (d) Hysteresis area for Control_SP_FA sample at $t=30$. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

In fact, throughout the literature there has been a contradiction on the accuracy of hysteresis area method. Even though, this method evaluates the amount of structural breakdown at high shear rates, it does not provide an insight about the structural breakdown (or build-up) at lower shear rates. Thus, there would be a need to quantify the thixotropy with additional approaches. Thixotropic materials would exhibit structural build-up which indicates an increase in their elastic modulus and static yield stress increase with the time [100]. To understand the static yield stress evolution by time, shear profiles were obtained by loading the samples at very low

shear rates (0.1s^{-1}) for 60 s. Figure 4.3 represents the static yield stress evolution for Control_SP and Control_SP_FA samples. The peak value obtained from these curves represents the static yield stress of the material and the decrease beyond the peak value indicates destructuration of the material at low shear rates. Table 4.2 summarizes the static yield stress values for Control_SP and Control_SP_FA samples. The analyses were done on triplicates of samples on each mix and samples belong to the same set of mix showed similar rheological profile. For simplicity one representative graph for each set of mix was shown in Figure 4.3 but the average values and standard deviation in Table 4.2 was obtained from triplicates of samples (See Appendix C for other trials). Similar to the previous observations, the static yield stress evolution after 30 min of rest was 50% lower in Control_SP_FA sample compared to Control_SP sample. To understand how these values actually affect the printability, Wangler et. al. [101] proposed a mathematical equation such as, the theoretical static yield stress of each layer should be $\tau_o = \rho h g \sqrt{3}$ where τ_o , is the yield stress, ρ is the density of the mix and h is the individual layer height. To print a stable cement-based element with a 15 mm layer height, the static yield stress should be approximately 350-400 Pa. Thus, both these mixtures require thickening require additional thixotropic agents to improve the robustness and structural build-up at rest. Another relevant parameter A_{thix} was also calculated for cement paste samples. A_{thix} is an indication of the stiffness of the material relating to the ability of a layer to carry the subsequent layers during 3D printing process.

The A_{thix} value calculated for the first 5 minutes was 0,21 Pa/s for and it was 0,1 Pa/s for control_SP_FA sample. The overall structuration rate is calculated as 0,24 Pa/s for Control_SP sample and it was 0,15 Pa/s for Control_SP_FA sample. This also proves that incorporation of fly ash reduced the structuration rate of cement paste.

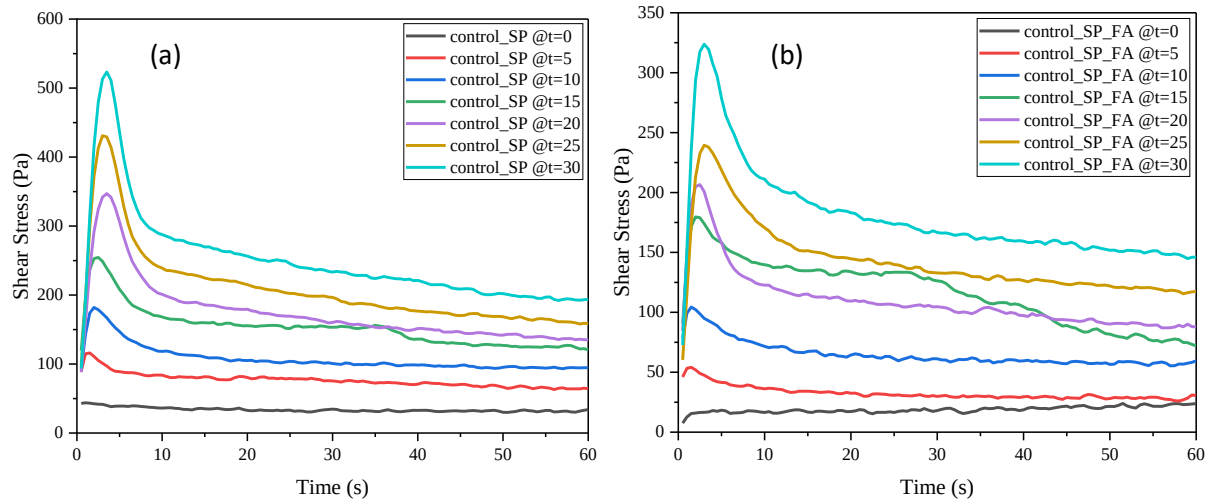


Figure 4.3: Shear stress (Pa) vs. time (s) graphs obtained at t=0,5,10,15,20,25,30 min. (a) shear profile for Control_SP sample at different time intervals (b) shear profile for Control_SP_FA sample at different time. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

Table 4.2: The average static yield stress values obtained from static shear rate model at t=0,10,20,30 for mixtures containing VMA.

Sample Name	time (min)	Average	
		Static τ_0	Std. Dev.
control_SP	0	36,3	9,2
	5	100,0	22,2
	10	172,0	23,7
	15	239,5	48,9
	20	308,5	56,7
	25	385,1	50,2
	30	474,4	52,4
control_SP_FA	0	17,6	6,3
	5	47,8	13,7
	10	89,5	23,0
	15	143,3	42,0
	20	171,7	39,9
	25	217,8	29,7
	30	281,6	51,7

At last but not the least, the structural breakdown and build-up in cement-based systems were evaluated by step method (Apparent viscosity model). The material was sheared at 2 different shear rates at 3 different stages. First, the material was subjected to a very low shear rate of 0.1 s^{-1} (simulating at rest conditions), then it was loaded at high shear rates (300 s^{-1}) and finally brought back to the rest conditions. Figure 4.4 shows the changes in apparent viscosities of control_SP and control_SP_FA samples at 3 different stages (Again only set of graphs were used

to represent the similar trends in triplicates of samples, See Appendix D for other trials). For both samples, there was a immediate decrease in Apparent viscosity upon removal of high shear and this was more pronounced in samples containing FA. While the Control-SP sample exhibit structural build-up within the following 5s of unloading, this duration was close to 10s for Control_SP_FA samples. Relatedly, the Apparent viscosity values for Control_SP and Control_SP_FA samples before the high shear loading was 280,5 mPa.s and 131,5 mPa.s, respectively. Upon recovery, the Apparent viscosity of Control_SP was 239,4 mPa.s and it was 103,3 mPa.s for Control_SP_FA sample. This corresponds to a recovery rate of 85% Control_SP and 76% for Control_SP_FA sample. As a conclusion, incorporation of 20% FA reduced the yield stress, viscosity and structuration rate of cement paste samples which was all expected due to the latent hydraulic behavior of the FA.

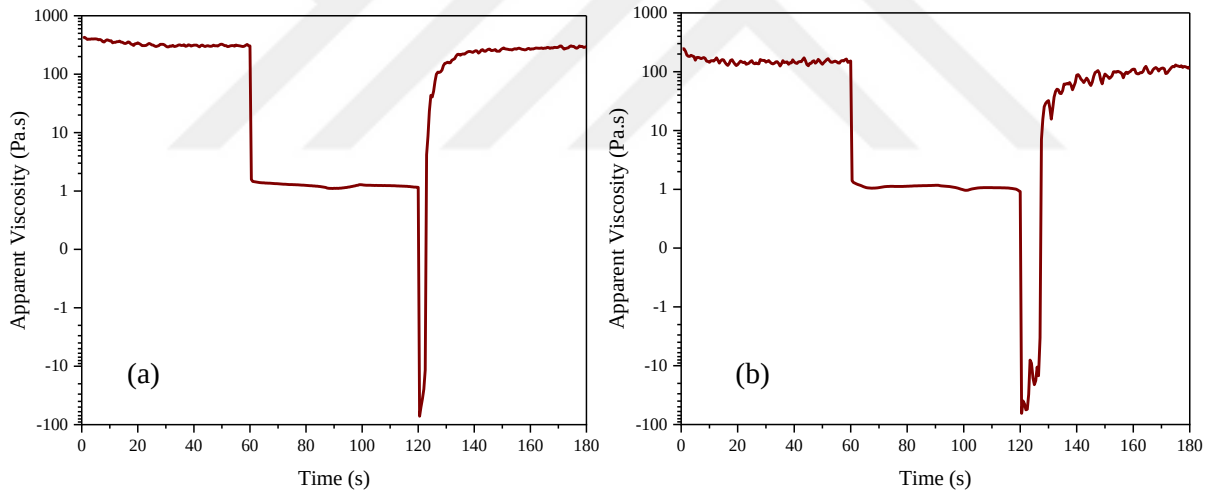
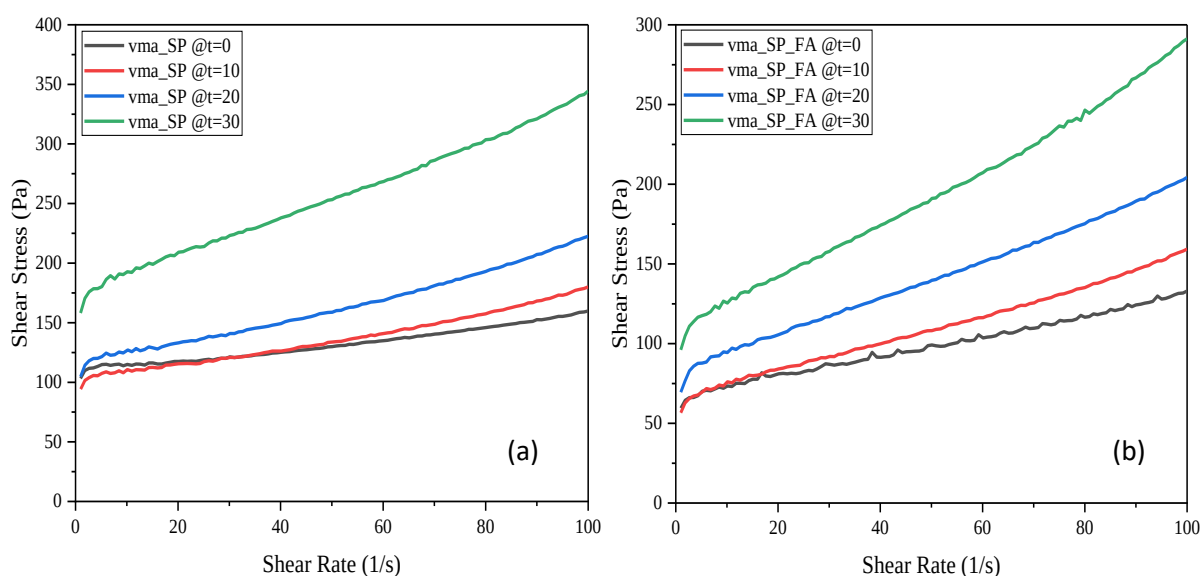


Figure 4.4: Effect of different shear rates on apparent viscosity of control samples. (a) Apparent viscosity for Control_SP sample at different time intervals (b) Apparent viscosity for Control_SP_FA sample at different time. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

The results obtained from control samples showed that there is a further need of thixotropic agents particularly for digital fabrication applications. A common approach to improve the printability of the mix is to use VMAs. Most VMAs improve the interaction with cement particles and improve flocculation. In particular, their efficiency depends on their molecular weight and absorbance on cement particles. In term of rheological properties, VMAs are expected to increase the yield stress as well as viscosity. Cellulose-ether or starch-ether derivatives such as welan gum and diutan gum are commonly used in cement-based materials to improve the yield stress [102]–[104]. In presence of most VMAs, shear-thinning behavior is preserved, which means the viscosity of the material still decreases with increasing shear rate [105]. Figure 4.5 represents the influence of a starch derived VMA (0.3% w/w cement) on rheological properties of cement paste. The analyses were done on triplicates of samples on each mix and samples belong to the same set of mix showed similar rheological profile. For simplicity one representative graph for each set of mix was shown in Figure 4.5 but the average values and standard deviation in Table 4.3 was obtained from triplicates of samples (See Appendix A for other trials).



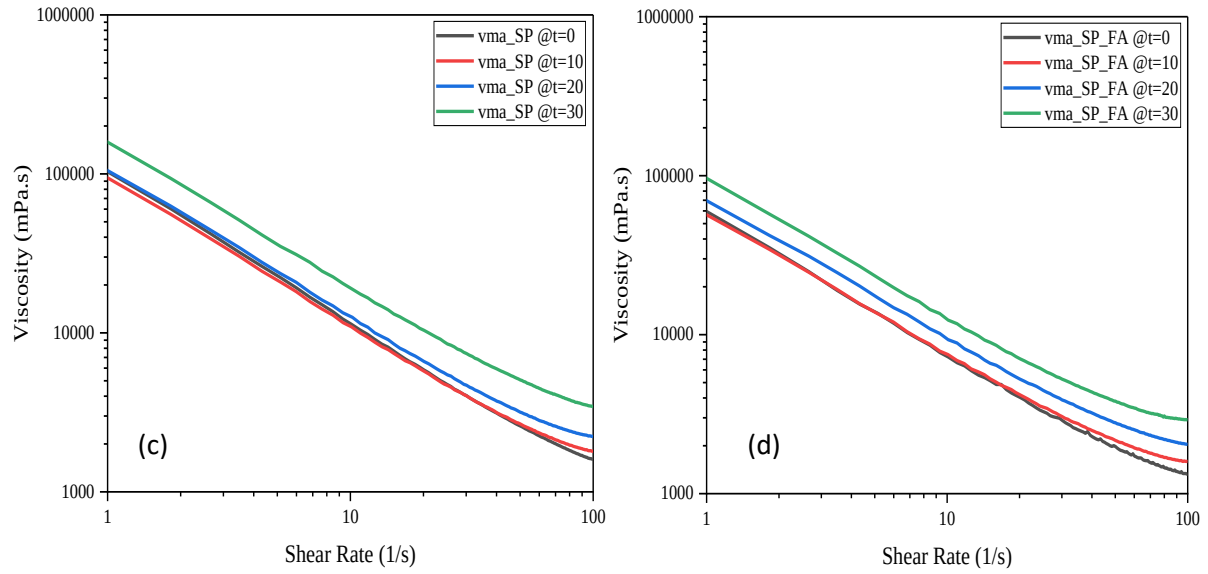


Figure 4.5: Shear Profiles of samples containing starch ether VMA (0.3% by w/w of cement) obtained from the increasing shear rate model. (a) shear profile for VMA_SP sample at different time intervals (b) shear profile for VMA_ SP_FA sample at different time intervals (c) Viscosity profile for VMA_SP sample at different time intervals (d) Viscosity profile for VMA_SP_FA sample at different time intervals. The profile was analyzed by H-B model using the down-curve of the hysteresis loop.

SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

Table 4.3: The average Herschel and Bulkley parameters (K , n and τ_0) and thixotropy values obtained from the area between the up and down curves obtained from increasing shear rate model at $t=0,10,20,30$ for mixtures containing starch ether VMA (0.3% by w/w of cement).

Sample Name	time (min)	Average				Thixotropy [Pa.s]
		K [Pa.s]	n	τ_0 [Pa]	τ_0 [%increase]	
vma_SP	0	0,0	1,8	155,4	0,0%	2376,0
	10	0,1	1,5	151,1	-3,1%	3918,9
	20	0,1	1,4	169,7	12,5%	3254,3
	30	0,6	1,2	215,9	29,5%	3076,7
vma_SP_FA	0	0,5	1,0	72,5	0,0%	1922,6
	10	0,5	1,1	79,5	9,9%	3739,8
	20	0,7	1,1	98,4	24,5%	4114,9
	30	0,6	1,2	133,2	36,4%	4810,9

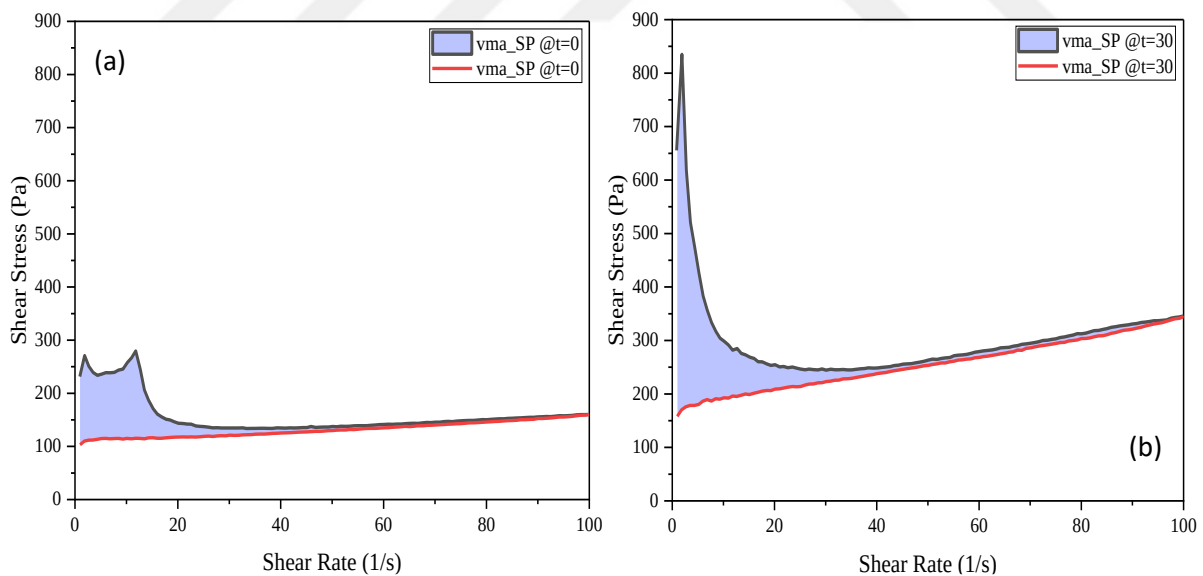
As mentioned above, VMAs can increase the yield stress without reducing the workability. This property enables an ease of extrusion at higher shear rates and an improved resistance of material deformation under its own weight at rest, which are essential for additive manufacturing. Herein, incorporation of VMAs lead to dynamic yield stress values in VMA_SP

and VMA_SP_FA samples 6 times larger compared to their counterpart neat control samples (Comparing Figure 4.1 and 4.5). In contrast, the consistency index, K , in VMA incorporated samples was almost 50% lower than control samples. This rheological behavior reflects the main characteristic of VMAs in general. In particular, VMAs can be absorbed on cement particles, bridge them and led to an increase in yield stress [4], [106]. In addition, some VMAs can reduce the bleeding since the long chain molecules of VMA stick to the water molecules, decrease their relative motions, and forms a gel, so increase the yield stress [103]. Their affinity with cement particles and ability to increase water retention were higher with increasing molecular weight [4]. Similarly, the incorporation of VMAs with 20% FA replacement (VMA_SP_FA) resulted with a lower yield stress compared to VMA_SP sample which is again attributed to FAs tendency to increase flowability accompanied by reducing early age strength (green strength).

In addition, the degree of shear-thinning was reduced, particularly in VMA_SP sample. The “ n ” flow index in H-B model is an indicator for if the material is shear-thinning ($n < 1$) or shear-thickening ($n > 1$). While Control_SP sample almost exhibit a Bingham behaviour with n -value averaged 1, the average n -value for VMA_SP sample is around 1.5. Even though the model is suggesting a shear-thickening behavior, Figure 4.5 still demonstrates a-shear thinning behavior. This might suggest that incorporation of 0.3% of VMA (w/w of cement) reduced the shear-thinning behavior, however increasing dosage of VMA might also induce shear-thickening behavior.

Interestingly, while the absolute dynamic yield stress values in samples containing VMAs were much higher than their counterpart control samples, the % change in dynamic yield stress with time still remained around 30%. A further analysis of thixotropy based on hysteresis area (Table 4.3) showed that even though the area enclosed between the up and down curve at $t=0$ was larger in VMA_SP sample compared to Control_SP sample, an opposite trend was observed at

t=30 min. Relatedly, the hysteresis area calculated in VMA_SP_FA samples was much larger compared to Control_SP_FA sample which indicated that the influence of VMAs on structural build-up was more pronounced in samples containing FA, where the thixotropic characteristics were already reduced due to presence of FA. VMAs contributed in a higher degree to the structural recovery of a more flowable sample. Structural build-up or recovery is the ability of the cement paste related to thixotropy which allows the material to flocculate and de-flocculate at different shear rates. Portland cement-based systems can exhibit an intrinsic thixotropy property, due to on-going hydration and flocculation of cement particles. However, agents such as FA, aggregates or some superplasticizers can reduce the particle-to-particle interaction in cementitious matrix and influences the recovery ability of the mixture. VMAs are much more affecting leading to a higher degree of particle-to-particle interaction in these mixes by overcoming the repelling forces on the cement particles.



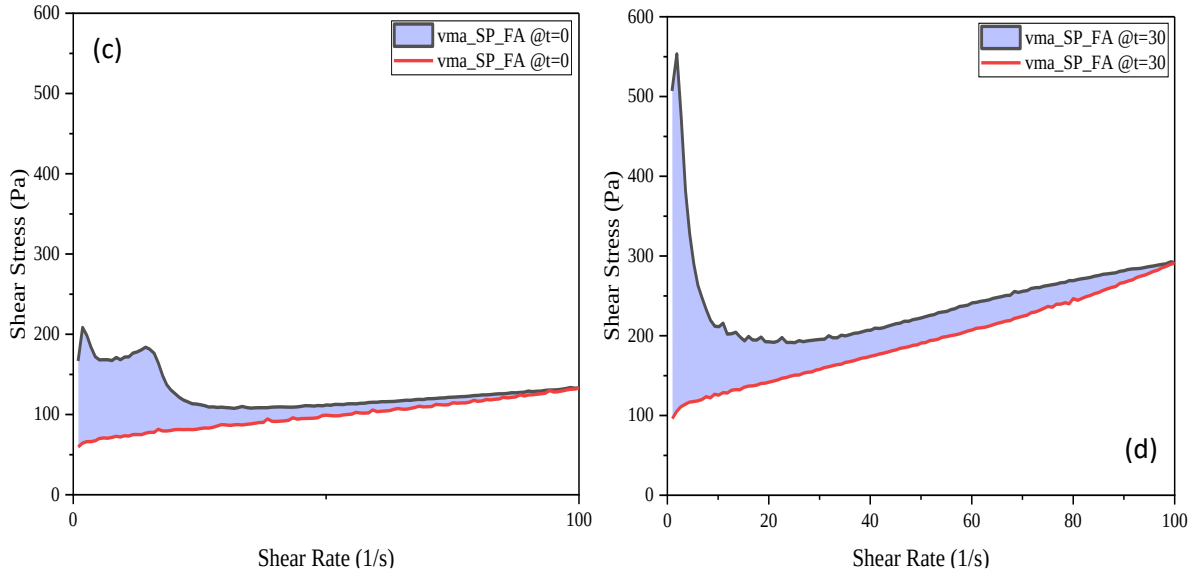


Figure 4.6: Hysteresis areas for VMA_SP and VMA_SP_FA mixture obtained at $t=0$ and 30 min. The areas are between the up and down curves, shown in blue color. (a) Hysteresis area for VMA_SP sample at $t=0$ (b) Hysteresis area for VMA_SP sample at $t=30$ (c) Hysteresis area for VMA_SP_FA sample at $t=0$ (d) Hysteresis area for VMA_SP_FA sample at $t=30$. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight); VMA: starch ether VMA (0.3% by w/w of cement)

The influence of VMAs on dynamic yield stress might influence the extrudability of the material. Depending on the printer type higher dynamic yield stress might induce clogging on the nozzle. In general, while the dynamic yield stress is an indicator of extrudability, the static yield stress is rather an indicative of early age strength development and buildability [85]. For printing applications, it is critical to have increasing static yield stress with time. Figure 4.7 represents the static yield stress evolution for VMA_SP and VMA_SP_FA samples. For simplicity one representative graph for each set of mix was shown in Figure 4.7 but the average values and standard deviation in Table 4.4 was obtained from triplicates of samples (See Appendix C for other trials).

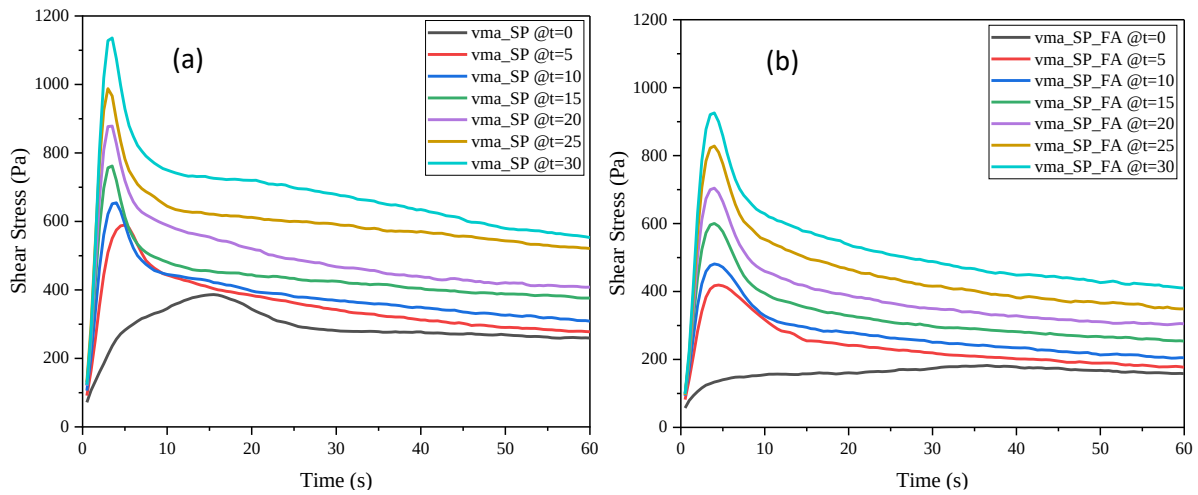


Figure 4.7: Shear stress (Pa) vs. time (s) graphs obtained at t=0,5,10,15,20,25,30 (a) shear profile for VMA_SP sample at different time intervals (b) shear profile for VMA_SP_FA sample at different time. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight); VMA: starch ether VMA (0.3% by w/w of cement)

Table 4.4: The average static yield stress values obtained from static shear rate model at t=0,10,20,30 for mixtures containing VMA (0.3% by w/w of cement). All mixes contain superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

Sample Name	time (min)	Average	
		Static τ_0	Std. Dev.
vma_SP	0	389,9	67,8
	5	611,1	46,1
	10	669,5	36,9
	15	786,5	24,1
	20	902,1	36,4
	25	1034,4	97,1
	30	1172,0	127,3
vma_SP_FA	0	182,2	77,9
	5	409,6	77,4
	10	466,5	80,3
	15	576,0	107,7
	20	691,1	136,2
	25	817,0	167,1
	30	917,7	169,2

As mentioned before, to print a stable cement-based element with a 15 mm layer height, the static yield stress should be approximately 350-400 Pa. While the analysis on control samples showed that the inherent thixotropic characteristic of cement paste was not enough to achieve this theoretical value, incorporation of VMAs enabled to provide static yield stress values at least 10 times larger than the control samples even at t=0. Relatedly, A_{thix} value calculated for VMA_SP sample from t=0 to t=5 min was 0,74 Pa/s and it was 0,76 Pa/s for VMA_SP_FA

sample. This showed that the structuration rate at the first 5 minutes of VMA_SP and VMA_SP_FA samples are almost the same. The overall structuration rate is calculated as 0,43 Pa/s for VMA_SP sample and 0,41 Pa/s for VMA_SP_FA sample. This shows that VMAs induce an immediate effect on thixotropy and the affect was less pronounced with time. Overall, incorporation of VMAs resulted with a significant increase on structural build-up of the cement-paste particularly in presence of FA. Since the measurements were done within the first 30 minutes of mixing, most of the effects induced by VMA is reversible and directly related to thixotropy rather than irreversible effects of hydration, like incorporation of an accelerator [107].

By definition, thixotropy is directly related to viscosity recovery. Thus, the structural break down and recovery of the cement paste can be attributed to the change of apparent viscosity at different shear rates. In 3D printing applications, the shape retention after extrusion is also related to the recovery of viscosity. Figure 4.8 represents the changes in apparent viscosities of VMA_SP and VMA_SP_FA samples at 3 different stages. Again only set of graphs were used to represent the similar trends in triplicates of samples (See Appendix D for all trials). Both 2 samples exhibited a shear-thining behavior at high shear-rates. In fact, incroporation of VMAs reduced the duration of rapid decrease in appearnrt viscosity upon unloading. This was attributed to incorporation of VMAs increase the flocculation of cement particles at rest resulting with a higher degree of structural recovery. Based on the analysis, the Apparent viscosity of VMA_SP was 2048,4 mPa.s before the 300 s^{-1} shear, it was around 1 Pa.s during the shearing period and recovered back to 1567 mPa.s. So, VMA_SP recovered 77% of its initial viscosity almost immediately after recovery. In fact, the Control_SP sample recovered 85% of its viscosity 5s after removal of the shear. Relatedly, Control_SP_FA sample recovered 76% of its viscosity 10s after unloading. However, for VMA_SP_FA sample, the viscosity before the 300 s^{-1} shear application is 1617,5 mPa.s and after it is 1122,3 mPa.s, which means the sample recovered

70% of its viscosity again almost right after unloading. Eventhough, the presence of VMAs resulted with slightly lower degree of strucutral recovery, the material responded the loading faster than the control sample.

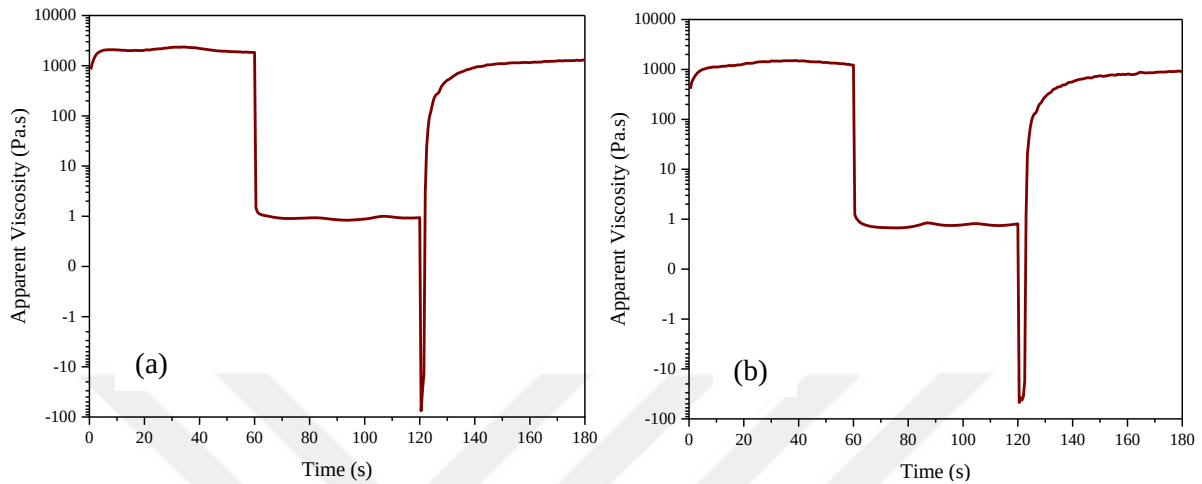


Figure 4.8: Effect of different shear rates on apparent viscosity of control samples. a) Apparent viscosity for VMA_SP sample at different time intervals (b) Apparent viscosity for VMA_SP_FA sample at different time. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight; VMA: starch ether VMA (0.3% by w/w of cement)

It should be noted that the kinematic involve during shearing is different than the kinematics involve during recovery phase. The initial structural build-up is mainly attributed to the formation of weak van der Waals forces due to agglomeration of cement particles which can be easily broken during shearing (or during extrusion). Upon, removal of the load a new set of bonds are build up very fast and incorporation of VMAs mainly increase the agglomeration of cement particles again since they have been already absorpbed on the particles. To understand the degree of structural build-up during recovery and to measure degree of flocculation, additional investigation like particle size analysis or in-situ microscopy have to be done.

4.2 Use of nano-montmorillonite as a VMA in cementitious materials

Previous work in the literature showed that even with a small amount of addition nano clays can improve the thixotropy of the cement-based matrices due to their electrostatic attraction. These nano sized clays having charged edges can induce attraction forces between cement particles resulting with a more stable microstructure and higher viscosity at rest. In addition, due to their very small particle size and higher specific surface area they can improve the packing between cement particles and increases the formation of van der Waals force which will increase the degree of structural build up, thus the degree of thixotropy in the system. The scope of this thesis is to understand the influence of various clays on rheology of cement paste which then could be adapted for 3D printing. There are various studies explaining the impacts of clays such as attapulgite, bentonite, sepiolite and kaolinite on rheological properties of cement-based materials. The results from these studies were promising and there is a need for further evaluation to extend the list of possible other type of clays. Therefore, another set of extensive rheological analysis was performed on samples containing surface-modified nano-montmorillonite (NM). Figure 4.9 and 4.10 represents the influence of NM (by 0.5% and 1% of w/w of cement respectively) on rheological properties of cement paste. The analyses were done on triplicates of samples on each mix and samples belong to the same set of mix showed similar rheological profile. A representative graph for each set of mix was shown in Figures 4.9 and 4.10 but the Table 4.4. summarizes the average values and standard deviation obtained from triplicates of samples (See Appendix A and B for all trials).

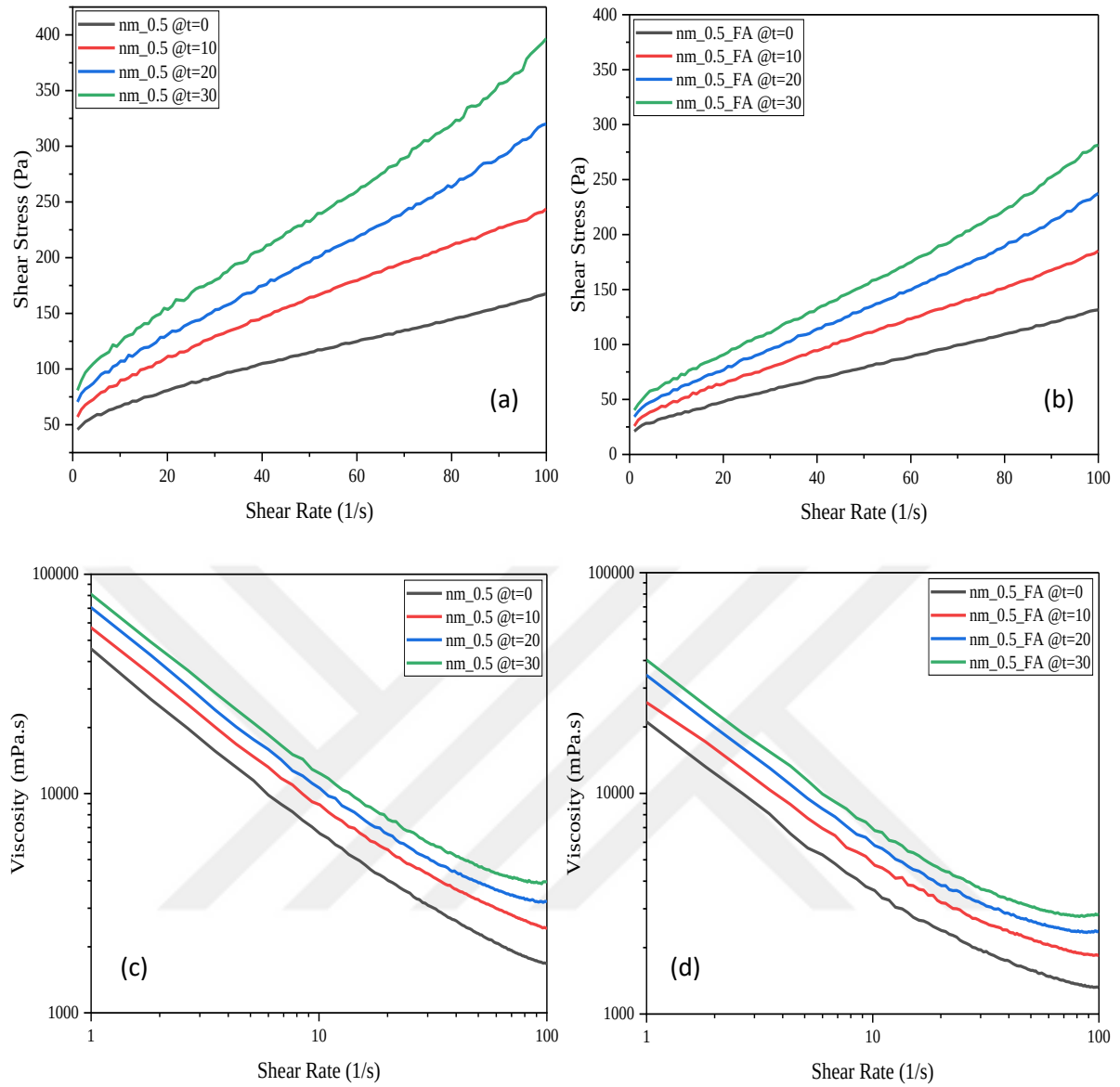


Figure 4.9: Shear Profiles of samples containing Nano-montmorillonite (NM) (0.5% by w/w of cement) obtained from the increasing shear rate model. (a) shear profile for NM_0.5 sample at different time intervals (b) shear profile for NM_0.5_FA sample at different time intervals (c) Viscosity profile for NM_0.5 sample at different time intervals (d) Viscosity profile for NM_0.5_FA sample at different time intervals. The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

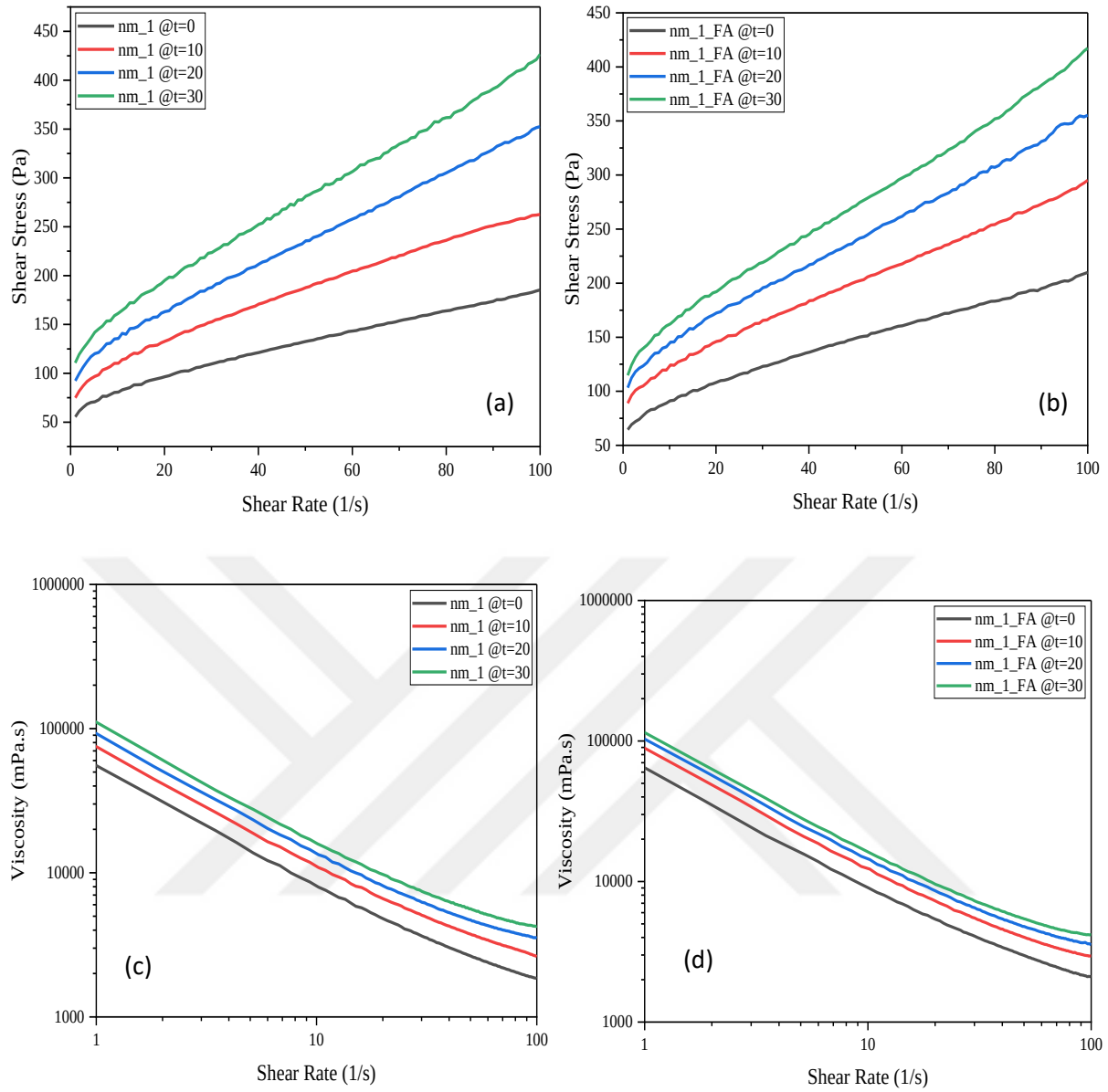


Figure 4.10: Shear Profiles of samples containing Nano- montmorillonite (NM) (1% by w/w of cement) obtained from the increasing shear rate model. (a) shear profile for NM_1 sample at different time intervals (b) shear profile for NM_1_FA sample at different time intervals (c) Viscosity profile for NM_1 sample at different time intervals (d) Viscosity profile for NM_1 _FA sample at different time intervals. The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

The shear profiles were obtained by analyzing the down-curve by using H-B model. While the dynamic yield stress obtained by incorporation of NM resulted with a higher dynamic yield stress compared to the counterpart control samples, it was lower than the dynamic yield stress of samples containing 0.3% VMA by weight of cement. However, as mentioned above the

working mechanism of clays are rather different than VMAs. VMAs are absorbed on cement particles and bridge them. This increases the flocculation and increase the yield stress without affecting the consistency index of the mix. However, the surface charge of nano clays (and NM) induces attraction forces between cement particles resulting with a more stable microstructure and higher viscosity at rest. In addition, they improve the thixotropic behaviour of the cement-based systems by increasing the formation of van der Waals force due to their very small particle size and higher specific surface. It should also be noted that the NM used in the mix is a surface modified nano clay which contains 25-30 wt. % trimethyl stearyl ammonium. This surface modification might alter the surface charge of the clays, reduce their tendency to swell and interfere with their affinity.

Incorporation NM resulted with a shear-thinning profile in the material similar to the control samples. The “n” flow index of the samples was still on par with control samples indicating a flow behaviour resembling the Bingham Model. So, while VMAs working mechanism influences the yield stress, the use of NMs would affect the viscosity as well as the thixotropic nature. Clays, exhibit shear thinning behaviour due to their repelling surface charges which creates a stiffening affect at rest and breakdown at shear [4]. Thus, it would be fair to compare K constant to compare the viscosity of the samples. Within this perspective, the H-B model K parameter obtained from samples containing NM was much higher than both control samples and samples containing VMA. Such that, the K constant in Control_SP sample ranged between 1.1 to 1.4, it was way lower in VMA_SP sample ranging between 0.5 and 0.7. Incorporation of 0.5% NM by weight of cement to Control_SP sample increased the K constant to a range between 2.6 to 4.4 and incorporation of 1% NM increased the K constant to 5.0-5.1. This is in line with the possible impacts of nano clays increasing the viscosity of the mix.

Table 4.5: The average Herschel and Bulkley parameters (K, n and τ_0) and thixotropy values obtained from the area between the up and down curves obtained from increasing shear rate model at $t=0,10,20,30$ for mixtures containing nano- montmorillonite (NM) All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); (0.5 and 1 % by w/w of cement).

Sample Name	time (min)	Average				Thixotropy [Pa.s]
		K [Pa.s]	n	τ_0 [Pa]	τ_0 [%increase]	
nm_0.5	0	3,5	0,8	47,5	0,0%	1250,1
	10	4,4	0,8	64,6	36,5%	1763,8
	20	2,6	1,0	90,1	39,6%	3806,8
	30	3,2	1,0	105,2	16,9%	4152,3
nm_0.5_FA	0	2,8	0,8	20,9	0,0%	1013,7
	10	1,7	1,0	35,0	89,4%	2256,6
	20	1,3	1,1	47,6	37,2%	2883,9
	30	1,4	1,1	57,6	20,9%	3306,6
nm_1	0	5,0	0,7	63,6	0,0%	1731,2
	10	5,0	0,8	85,5	34,5%	1854,0
	20	5,2	0,8	107,2	26,2%	2683,9
	30	5,1	0,9	126,4	18,0%	3247,1
nm_1_FA	0	4,0	0,8	48,2	0,0%	1396,9
	10	3,2	0,9	74,1	55,3%	2925,3
	20	3,0	1,0	94,1	28,2%	3807,3
	30	2,8	1,0	110,3	17,6%	5199,7

Another impact of use of nano clays (NM) is their impact on thixotropy. A further analysis of thixotropy based on hysteresis area (Figure 4.11 and 4.12) showed that incorporation NM even at 0.5% of cement weight significantly increased the are hysteresis area compared to counterpart control samples. While the hysteresis area calculated for NM_0.5 at $t=0$ and $t=10$ min was 50% less than what was obtained in VMA_SP sample, there was a sudden shift in structural build up upon 20 minutes at rest. Such that, the hysteresis area calculated for NM_0.5 at $t=20$ and $t=30$ min was approximately 50% more than what was obtained in VMA_SP sample. This indicates that VMAs actually impact the thixotropy right after mixing and NM rather exhibits a more time dependent mechanism. Increasing NM content to 1% also enlarged the area enclosed between up and down curve compared to control samples, particularly in presence of fly-ash.

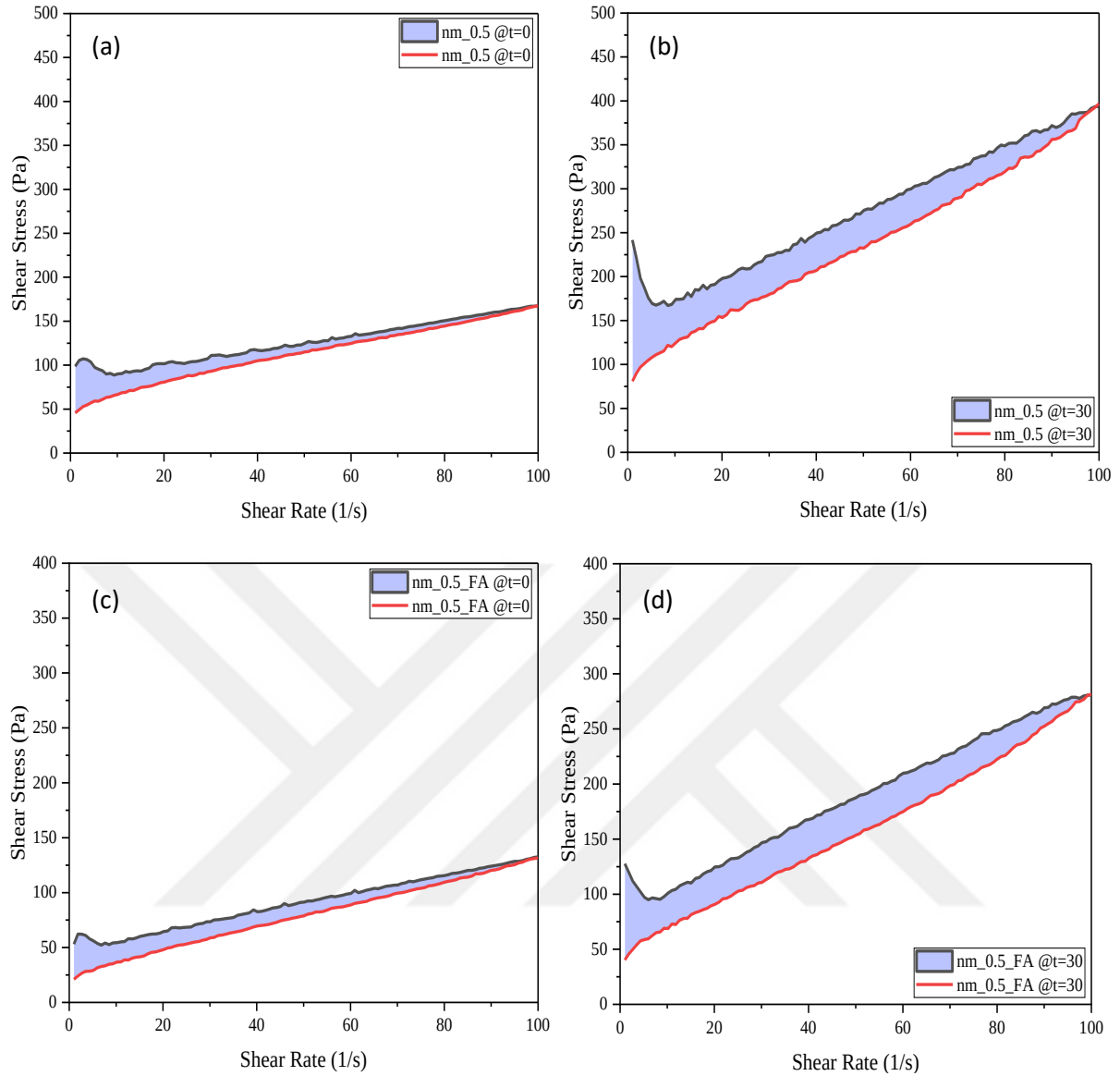


Figure 4.11: Hysteresis areas for NM_0.5 and NM_0.5_FA mixtures obtained at $t=0$ and 30 min. The areas are between the up and down curves, shown in blue color. (a) Hysteresis area for NM_0.5 sample at $t=0$ (b) Hysteresis area for NM_0.5 sample at $t=30$ (c) Hysteresis area for NM_0.5_FA sample at $t=0$ (d) Hysteresis area for NM_0.5_FA sample at $t=30$. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (0.5% by w/w of cement)

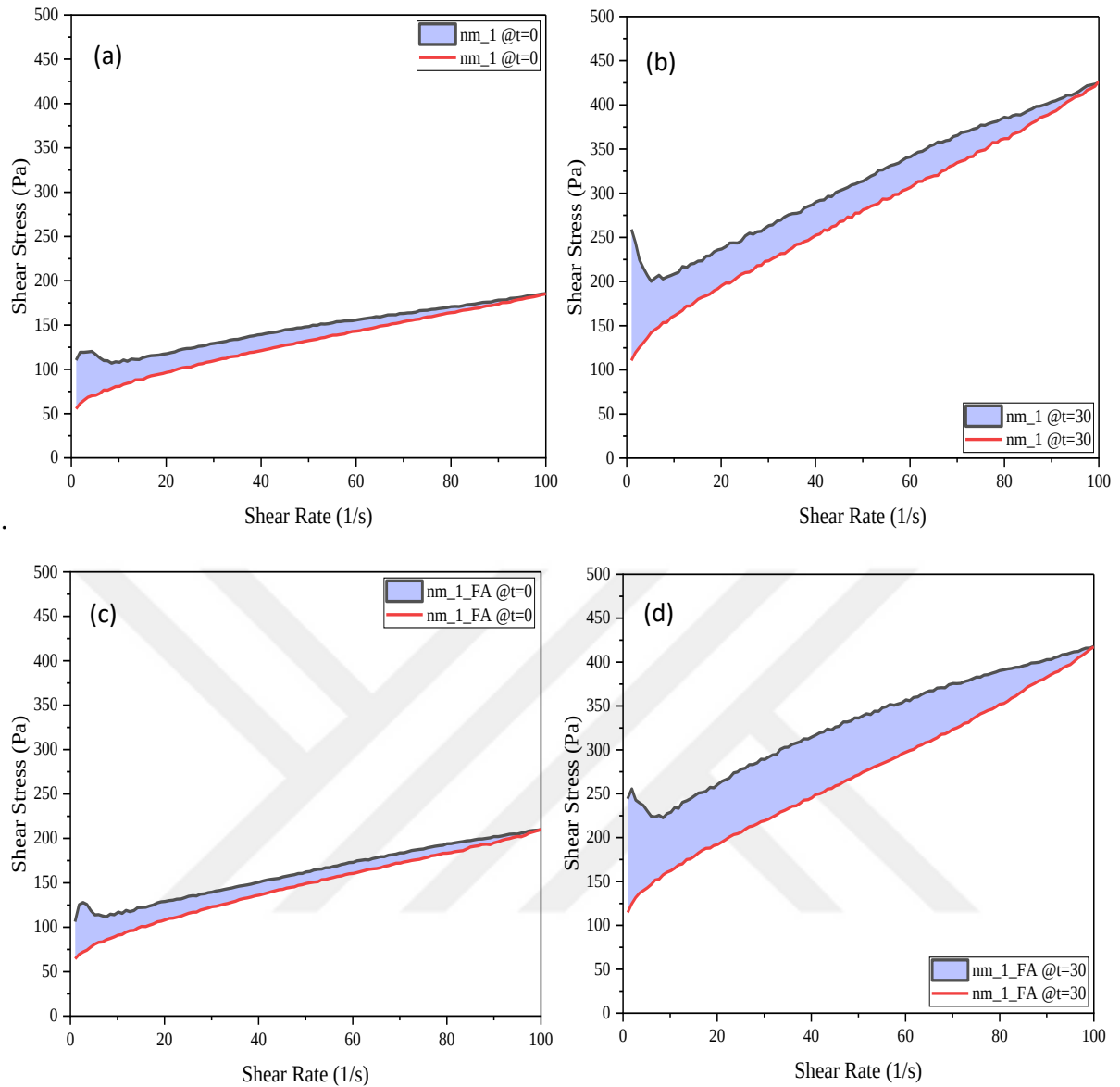


Figure 4.12: Hysteresis areas for NM_1 and NM_1_FA mixtures obtained at $t=0$ and 30 min. The areas are between the up and down curves, shown in blue color. (a) Hysteresis area for NM_1 sample at $t=0$ (b) Hysteresis area for NM_1 sample at $t=30$ (c) Hysteresis area for NM_1_FA sample at $t=0$ (d) Hysteresis area for NM_1_FA sample at $t=30$. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (1% by w/w of cement)

Considering that, NM increases the structural build up at rest, characterisation of static yield stress evolution with time would enable a more accurate understanding of the structural build-up rate. Figure 4.13 represents the static yield stress evolution for samples containing NM. A representative graph for each set of mix was shown in Figure 4.7, but the average values

and standard deviation in Table 4.6 was obtained from triplicates of samples (See Appendix C for all other trials).

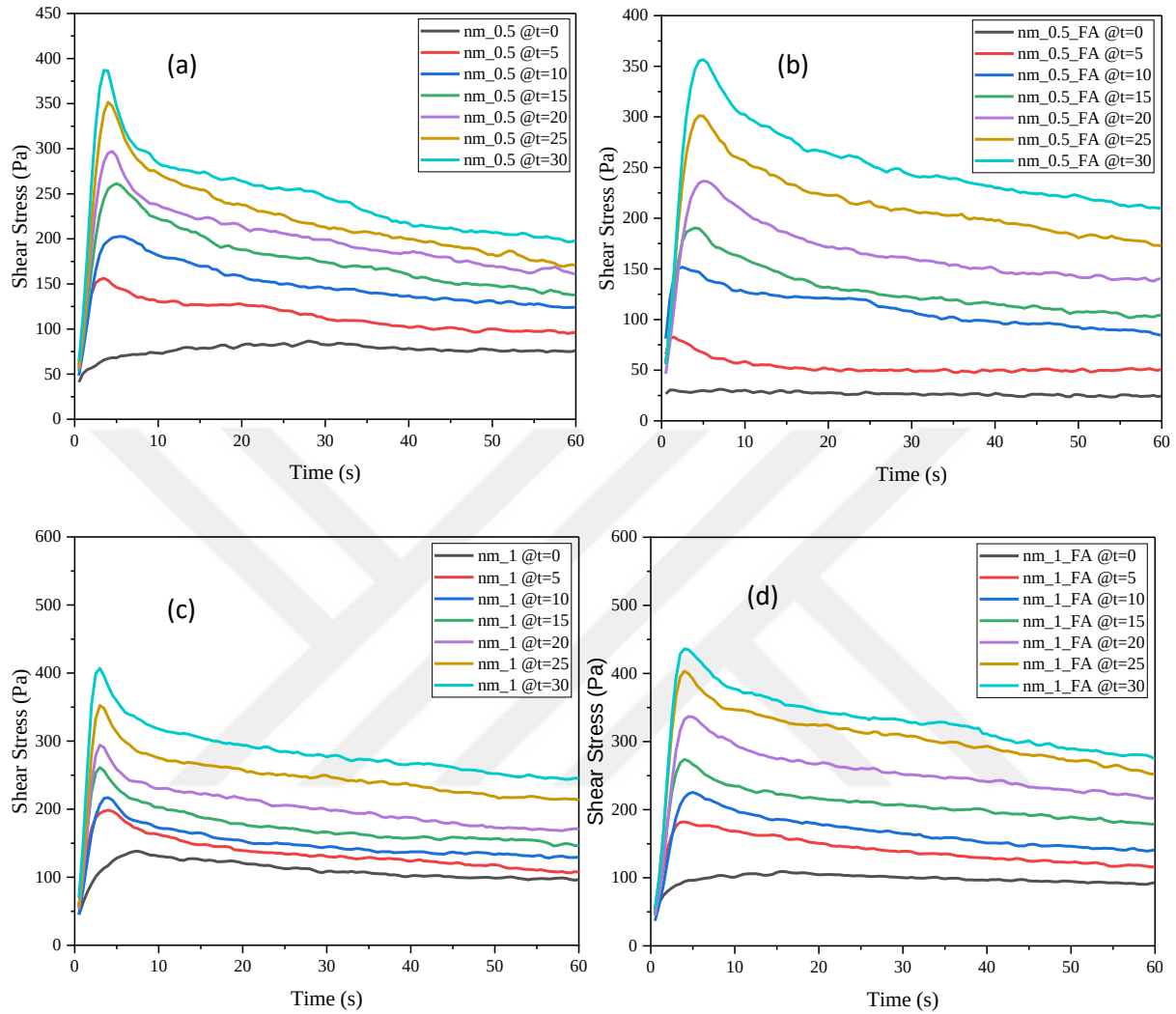


Figure 4.13: Shear stress (Pa) vs. time (s) graphs obtained at t=0,5,10,15,20,25,30 (a) shear profile for NM_0.5 sample at different time intervals (b) shear profile for NM_0.5_FA sample at different time (c) shear profile for NM_1 sample at different time intervals (d) shear profile for NM_1_FA sample at different time intervals. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (0.5 and 1% by w/w of cement)

A similar trend with H-B model evaluations was also observed such that incorporation of NM by 0.5% of cement weight increased the static yield stress compared to Control_SP samples. However, this impact was only pronounced during the first 10 minutes. This might indicate that NMs provided a higher degree of packing at first which increases the static yield stress rather

than actually creating a structuration. However, the influence of 0.5% NM replacement was more pronounced in NM_0.5_FA sample where the counterpart control sample (Control_SP_FA) was a low thixotropic material. In this case, incorporation of NM not only increase the static yield stress within the first 10 minutes, it also lead to a higher rate of static yield stress evolution with time. Increasing the NM content to 1% slightly increased the static yield stress evolution in NM_1 sample compared to NM_0.5.

Table 4.6: The average static yield stress values obtained from static shear rate model at t=0,10,20,30 for mixtures containing Nano-montmorillonite (NM-0.5 and 1% by w/w of cement). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

Sample Name	time (min)	Average	
		Static τ_0	Std. Dev.
nm_0.5	0	54,6	16,4
	5	134,3	30,0
	10	193,0	18,9
	15	243,4	27,5
	20	296,4	32,5
	25	349,4	17,6
	30	392,7	33,4
nm_0.5_FA	0	32,8	10,1
	5	89,0	23,5
	10	144,9	30,1
	15	198,7	31,1
	20	242,8	51,6
	25	306,1	78,6
	30	357,6	106,8
nm_1	0	136,2	28,2
	5	214,8	41,2
	10	257,6	49,8
	15	319,6	71,6
	20	350,0	73,9
	25	398,1	100,7
	30	454,2	97,2
nm_1_FA	0	85,4	20,4
	5	166,2	25,6
	10	225,8	29,8
	15	287,1	38,0
	20	344,1	36,6
	25	401,6	37,5
	30	440,1	30,2

Table 4.7 summarizes the overall change in static yield stress with time and A_{thix} values for all samples tested up to this point. Even though, incorporation of NM (NM_0.5 and NM_1 samples) improved the time dependent evolution of static yield stress compared to VMA_SP sample, the A_{thix} value still remained considerably lower. It should be noted that the % change in static yield stress is calculated by taking the relative difference of static yield stresses such as for 10 min NM_0.5 sample it was calculated as $(193-134.3)/134.3\%$, so it is a time independent ratio. However, A_{thix} value is the rate of change in static yield stress in a defined period, and it is 300s in this case. So, A_{thix} value for 10 min NM_0.5 sample was calculated as $(193-134.3)/300s$. The relatively high A_{thix} value for VMA_SP and VMA_SP_FA samples were then followed by sudden change to 0.19 Pa.s and then followed by an increasing trend. A similar trend with less pronounced decay was also observed in samples containing NM. However, both control samples exhibited an increasing A_{thix} value. A_{thix} value for Control_SP sample was almost constant through the 30-minute testing interval and Control_SP_FA exhibited an increasing A_{thix} value at least for the first 20 minutes of analysis. The different trend in samples containing VMA and NM might indicate that there is a higher degree of restoration of structure disturbed after pre-shear not actually reflecting the thixotropic nature of the material.

Table 4.7: The comparative relative static yield stress change (e.g., the % change in static yield stress at $t=5$ min wrt to static yield stress at $t=0$) with time and A_{thix} values for cement paste samples

CHANGE IN STATIC YIELD STRESS in 5 min REST INTERVALS								
Time at rest (min)	Control_SP	VMA_SP	NM_0.5	NM_1	Control_SP_FA	VMA_SP_FA	NM_0.5_FA	NM_1_FA
0-5	141%	57%	146%	58%	117%	125%	171%	95%
10	7%	10%	44%	20%	68%	14%	63%	36%
15	106%	17%	26%	24%	83%	23%	37%	27%
20	16%	15%	22%	10%	-5%	20%	22%	20%
25	-11%	15%	18%	14%	-26%	18%	26%	17%
30	4%	13%	12%	14%	74%	12%	17%	10%
A_{thix} (Pa/s)								
Time at rest (min)	Control_SP	VMA_SP	NM_0.5	NM_1	Control_SP_FA	VMA_SP_FA	NM_0.5_FA	NM_1_FA
0-5	0,21	0,74	0,27	0,26	0,10	0,76	0,19	0,27
5-10	0,24	0,19	0,20	0,14	0,14	0,19	0,19	0,20
10-15	0,23	0,39	0,17	0,21	0,18	0,37	0,18	0,20
15-20	0,23	0,39	0,18	0,10	0,09	0,38	0,15	0,19
20-25	0,26	0,44	0,18	0,16	0,15	0,42	0,21	0,19
25-30	0,30	0,46	0,14	0,19	0,21	0,34	0,17	0,13

As mentioned above, the influence of clays is more pronounced in terms of change in viscosity. Figure 4.14 represents the results of a 3-stage step analysis performed at 2 different shear rates. One particular difference of incorporation of NM compared to control samples and mixes containing VMA is the rapid recovery upon unloading, particularly samples that do not contain FA. Table 4.8 summarizes the % recovery in apparent viscosity before and after shear loading for all samples. Both change in yield stress and the recovery upon shear-thinning response is an indicative of thixotropy. While VMA are more effective in terms of increasing the rate of static yield stress evolution, NMs provide higher structural recovery upon shear-thinning behavior. Such that 1%NM addition to FA amended cement paste almost provided a full recovery in Apparent viscosity. As so, both control paste samples and samples containing NM exhibited a higher thixotropy compared to samples containing VMA which could be due to the symbiosis affect to NM and cement particles built up a network that rapidly increased the viscosity of the mixture. The recovery kinetics after shearing is completely different from the breakdown kinetics during shearing. While VMAs increase the yield stress by steric hindrance and their high molecular weight, NM influences the kinetics by their opposite surface charges. Thus, providing efficiency in structural build-up both in terms of increase in static yield stress evolution and apparent viscosity recovery.

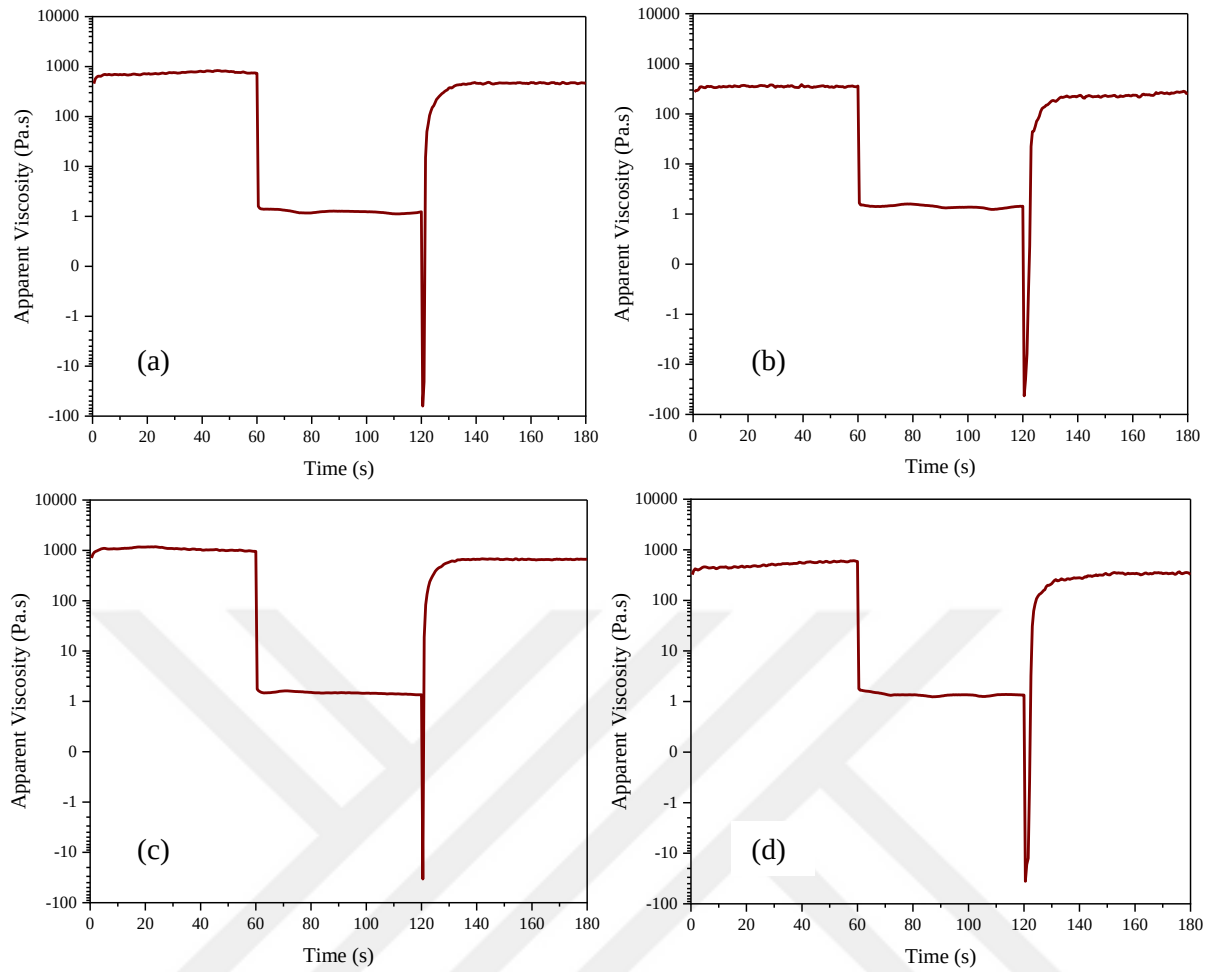


Figure 4.14: Effect of different shear rates on apparent viscosity of NM containing samples. a) Apparent viscosity for NM_0.5 sample (b) Apparent viscosity for NM_0.5_FA sample (c) Apparent viscosity for NM_1 sample (d) Apparent viscosity for NM_1_FA sample. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight; NM: Nano-montmorillonite (0.5% and 1% by w/w of cement)

Table 4.8: The comparative change in apparent viscosity before and after shear loading for cement paste samples, where Interval #1 describes the shearing period before shearing in 300s^{-1} and Interval #2 describes the shearing period after shearing in 300s^{-1}

	Apparent Viscosity values at constant shear [mPa.s]					
	control_SP	nm_0.5	nm_1	sep_0.5	sep_1	vma_SP
Interval #1	280,5	733,2	881,0	298,4	1223,3	2048,4
Interval #2	239,4	455,0	621,4	254,1	855,3	1567,1
%recovery	85%	62%	71%	85%	70%	77%
	control_SP_FA	nm_0.5_FA	nm_1_FA	sep_0.5_FA	sep_1_FA	vma_SP_FA
Interval #1	131,5	300,5	603,2	112,0	622,7	1617,5
Interval #2	103,3	226,4	442,4	81,1	536,2	1122,3
%recovery	79%	75%	73%	72%	86%	69%

4.3 Influence of sepiolite on rheological performance of cementitious systems

In nature clays can exist as having a layered microstructure like montmorillonite or as fibers in nanometre thickness. So, the clays can be either layered or fibrous. Through the literature, incorporation of fibrous nano attapulgite has been found effective to increase the static yield stress and rebuilding kinetics [4], [77]. Attapulgite is also known as palygorskite is a phyllosilicate clay, commonly found in U.S.A. An alternative to attapulgite can be another fibrous phyllosilicate clay can be sepiolite. In fact, Turkey has the largest sepiolite reserves in the world. It is hypothesized that sepiolite can improve the rheology of cement paste not only its opposing surface charges but also can provide a compactness because of its micro-fibrous microstructure. Sepiolite is cheaper compared to both cement and NM. There has been a little research done on possible use of sepiolite as a rheology modifier in cementitious materials, and it is still unknown if this cement-paste can actually be adapted to 3D printing. Figure 4.15 and 4.16 represents the influence of sepiolite (by 0.5% and 1% of w/w of cement respectively) on rheological properties of cement paste. The analyses were done on triplicates of samples on each mix and samples belong to the same set of mix showed similar rheological profile (See Appendix A and B for all other trials). A representative graph for each set of mix was shown in Figures 4.15 and 4.16 but the Table 4.9 summarizes the average values and standard deviation obtained from triplicates of samples.

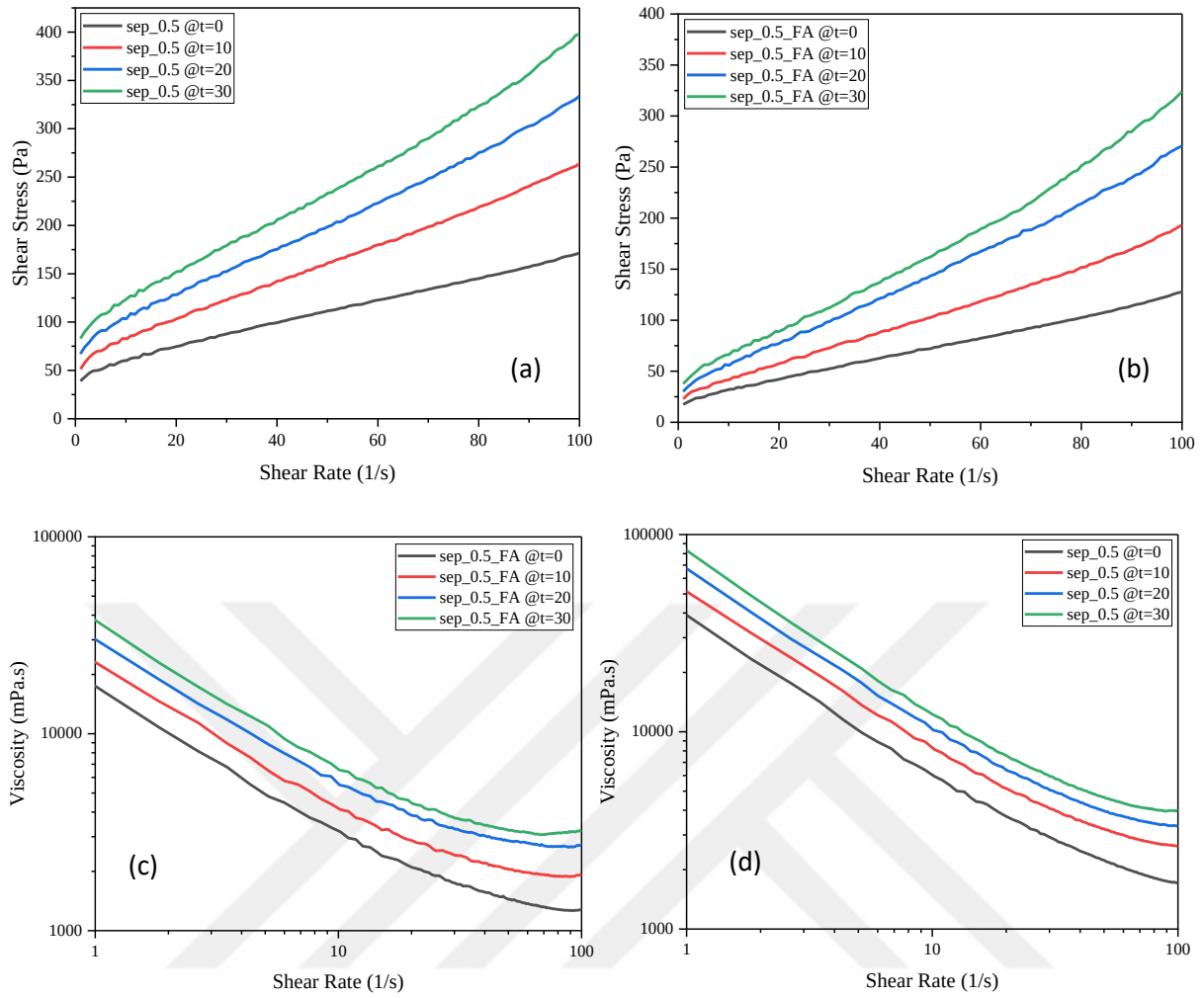


Figure 4.15: Shear Profiles of samples containing sepiolite (SEP) (1% by w/w of cement) obtained from the increasing shear rate model. (a) shear profile for SEP_0.5 sample at different time intervals (b) shear profile for SEP_0.5_FA sample at different time intervals (c) Viscosity profile for SEP_0.5 sample at different time intervals (d) Viscosity profile for SEP_0.5_FA sample at different time intervals. The profile was analyzed by H-B model using the down-curve of the. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

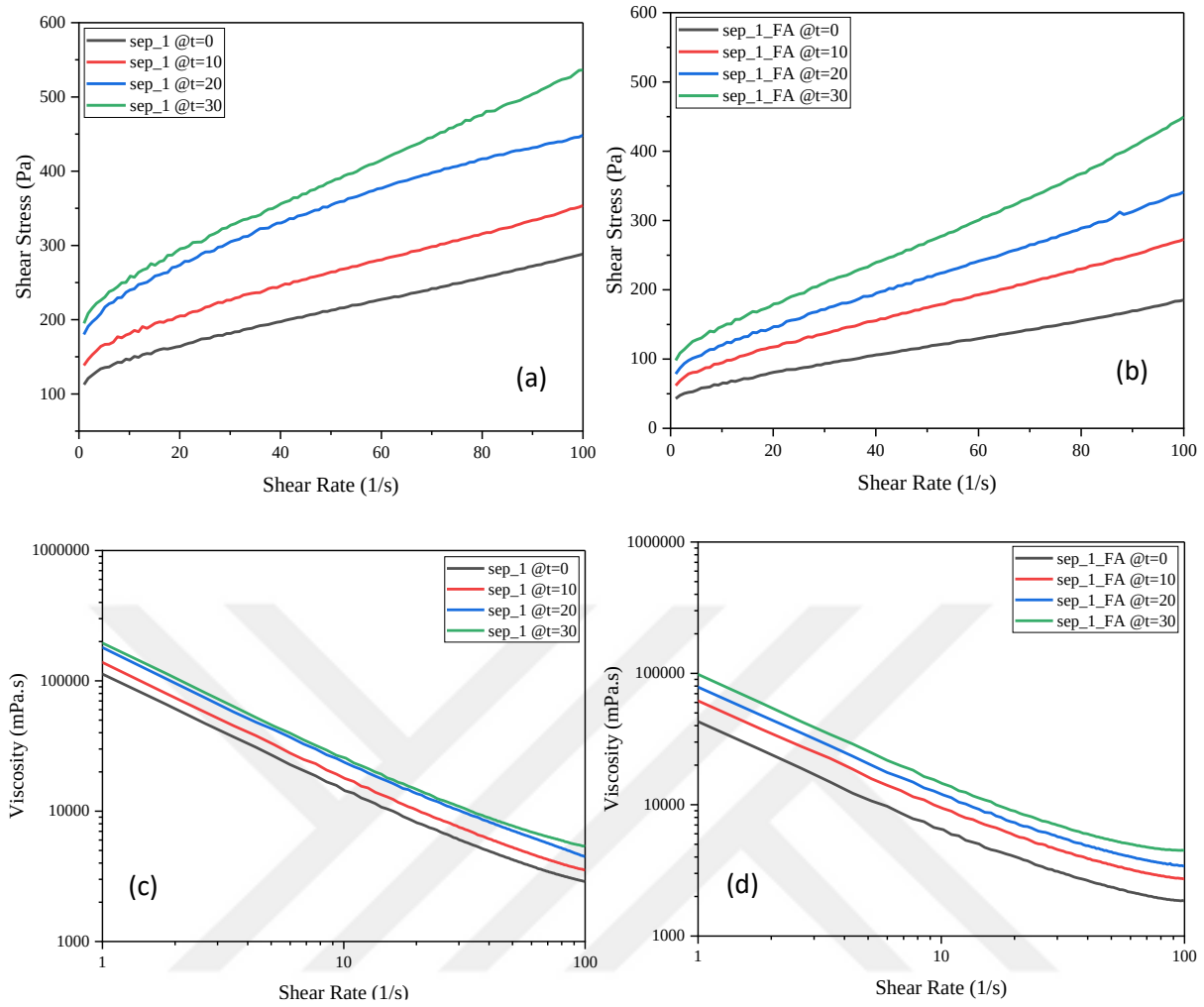


Figure 4.16: Shear Profiles of samples containing sepiolite (SEP) (1% by w/w of cement) obtained from the increasing shear rate model. (a) shear profile for SEP_1 sample at different time intervals (b) shear profile for SEP_1_FA sample at different time intervals (c) Viscosity profile for SEP_1 sample at different time intervals (d) Viscosity profile for SEP_1_FA sample at different time intervals. The profile was analyzed by H-B model using the down-curve of the. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

The shear profiles were obtained by analyzing the down-curve by using H-B model. Incorporation of 0.5% sepiolite (SEP_0.5) by weight of cement did not have any affect in terms of increasing the dynamic yield stress and thixotropy compared to its counterpart control sample (Control_SP). The results obtained from samples containing NM showed that influence of NM was more pronounced in samples containin 20% FA which has lower thixotropic characteristics. Figure 4.16 summarizes the H-B parameters calculated from shear profiles obtained from cement paste samples containing 20% FA replacement. Within this perspective,

use of 1% sepiolite in the mix resulted with a rheological performance on par with incorporation of VMAs. In fact, the highest dynamic yield stress values were obtained by incorporation of 1% sepiolite addition by weight of cement. It should also be noted that these samples (VMA_SP_FA and SEP_1_FA) contain more superplasticizers to provide the same slump with Control_SP. Otherwise, it was not possible to obtain a flowable mix with a lower dosage of superplasticizer.

Table 4.9: The average Herschel and Bulkley parameters (K , n and τ_0) and thixotropy values obtained from the area between the up and down curves obtained from increasing shear rate model at $t=0,10,20,30$ for mixtures containing SEP.

	time (min)	Average				Thixotropy [Pa.s]
		K [Pa.s]	n	τ_0 [Pa]	τ_0 [%increase]	
sep_0.5	0	2,3	0,8	35,4	0,0%	1462,3
	10	1,6	1,0	52,4	48,5%	2079,6
	20	1,8	1,0	65,9	25,8%	2844,7
	30	1,9	1,1	78,9	19,3%	4539,4
sep_0.5_FA	0	1,3	1,0	16,8	0,0%	1128,7
	10	1,0	1,1	26,0	57,1%	2491,3
	20	1,1	1,2	34,9	33,9%	3015,0
	30	0,9	1,2	45,4	30,5%	3915,3
sep_1	0	4,9	0,8	100,9	0,0%	1458,0
	10	6,6	0,8	127,1	27,7%	2865,9
	20	12,1	0,7	149,9	18,5%	1902,4
	30	6,8	0,8	176,7	17,7%	5085,6
sep_1_FA	0	2,5	0,9	72,9	0,0%	2101,0
	10	4,0	0,9	99,4	38,8%	4022,9
	20	4,4	0,9	119,0	20,7%	4232,3
	30	3,9	1,0	139,5	18,9%	5825,2

Generally, fibrous sepiolite particles can yield high viscosity values particularly at low solid concentrations by inducing higher flocculation efficiency [93]. But, this might not be the case in low w/c mixes like in this study. Similar to NM, the influence of 1% of sepiolite to the mix were more pronounced in terms of increasing the consistancy index, K which is related to the viscosity of the system. In addition, the flow index “ n ” for sepiolite containing samples were also close to 1 which indicates again indicates a shear-thining behavior resembling Bingham model.

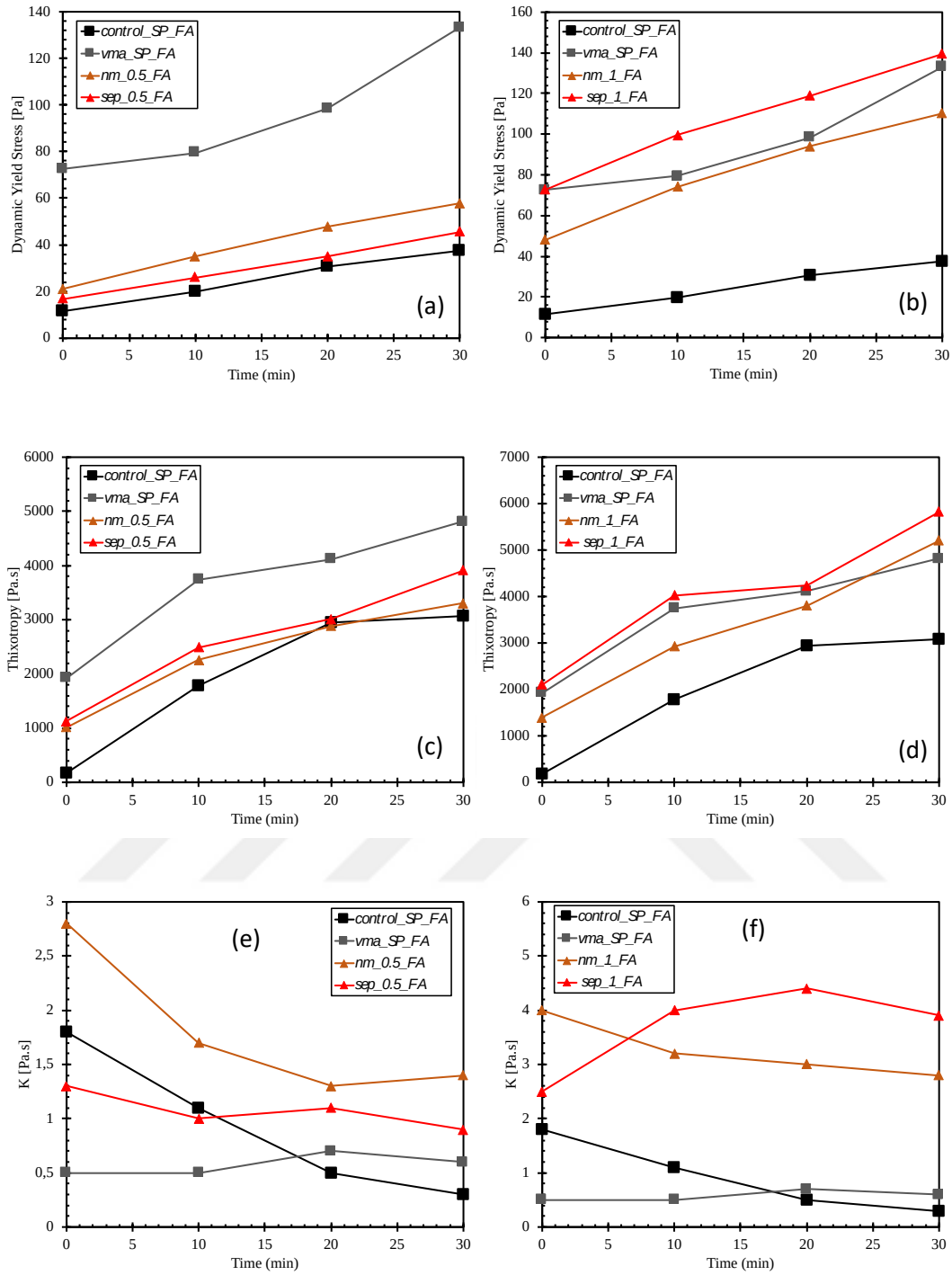


Figure 4.16: Comparative evaluation of Herschel and Bulkley parameters (K and τ_0) and thixotropy values obtained from hysteresis area at different time intervals (a) dynamic yield stress comparison for 0.5% NM and sepiolite addition (b) dynamic yield stress comparison for 1% NM and sepiolite addition (c) hysteresis area comparison for 0.5% NM and sepiolite addition (d) hysteresis area comparison for 1% NM and sepiolite addition (e) Consistency index, K , comparison for 0.5% NM and sepiolite addition (f) Consistency index, K , comparison for 1% NM and sepiolite addition

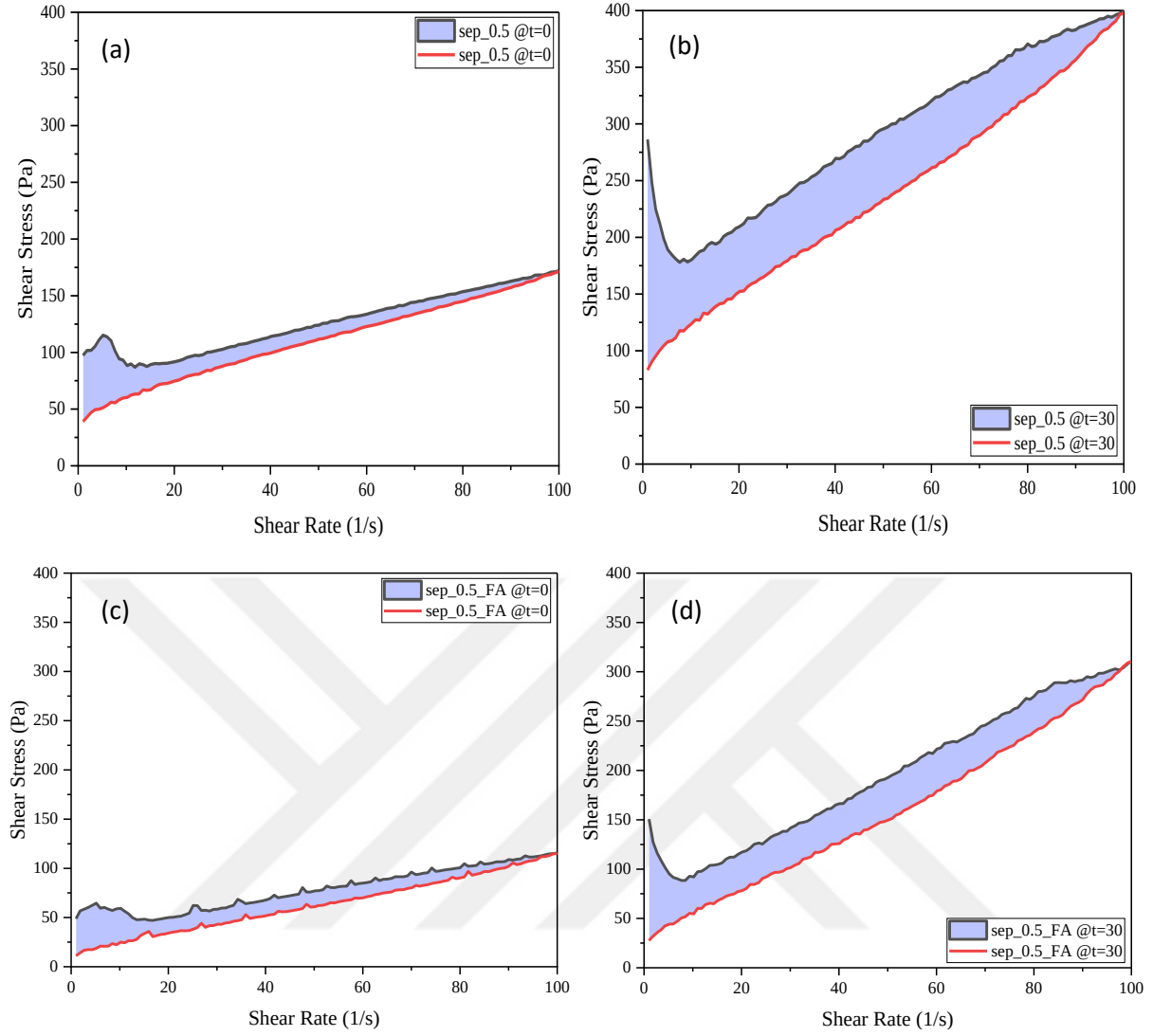


Figure 4.17: Hysteresis areas for SEP_0.5 and SEP_0.5_FA mixtures obtained at $t=0$ and 30 min. The areas are between the up and down curves, shown in blue color. (a) Hysteresis area for SEP_0.5 sample at $t=0$ (b) Hysteresis area for SEP_0.5 sample at $t=30$ (c) Hysteresis area for SEP_0.5_FA sample at $t=0$ (d) Hysteresis area for SEP_0.5_FA sample at $t=30$. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5% by w/w of cement)

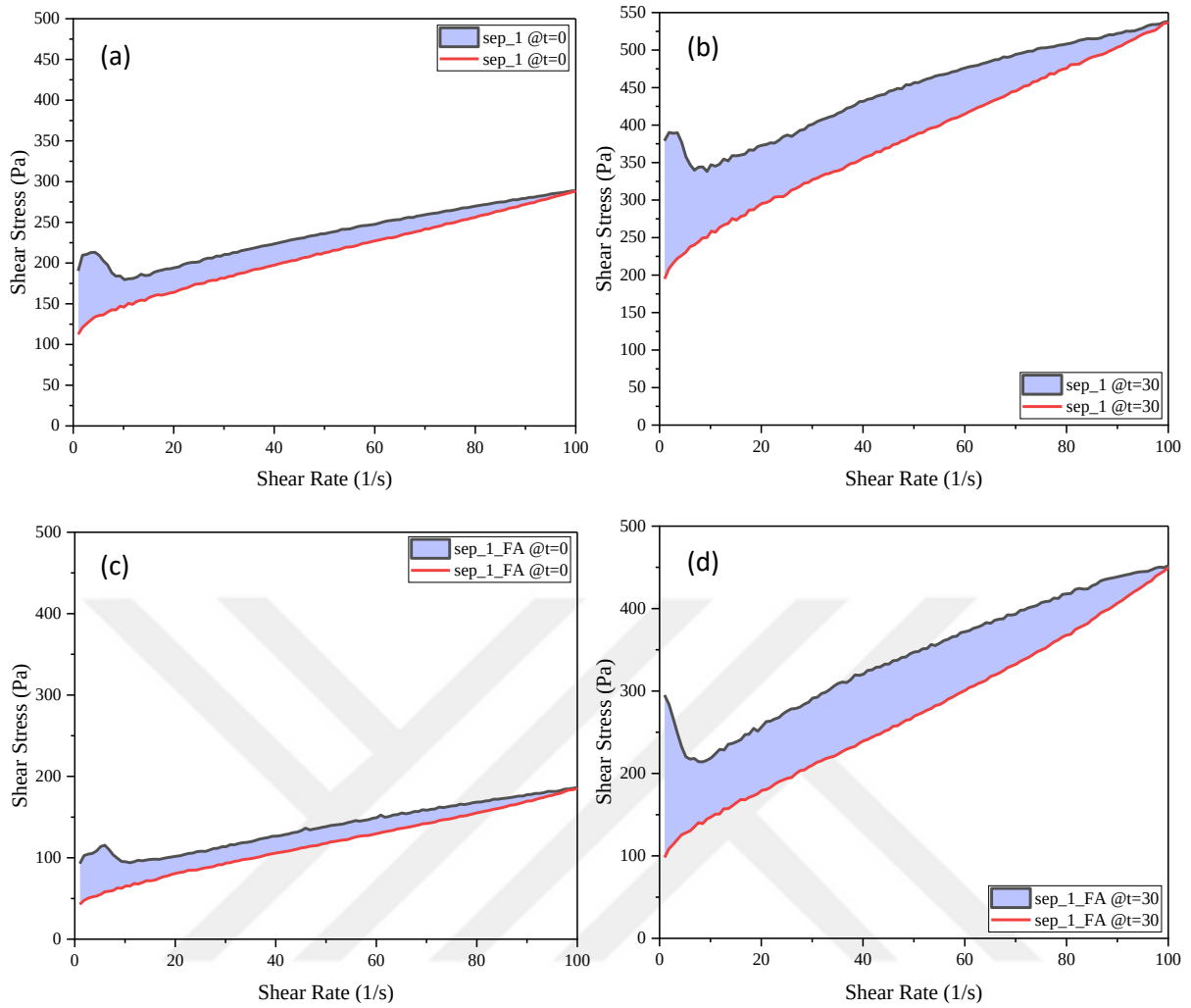


Figure 4.18: Hysteresis areas for SEP_1 and SEP_1_FA mixtures obtained at $t=0$ and 30 min. The areas are between the up and down curves, shown in blue color. (a) Hysteresis area for SEP_1 sample at $t=0$ (b) Hysteresis area for SEP_1 sample at $t=30$ (c) Hysteresis area for SEP_1_FA sample at $t=0$ (d) Hysteresis area for SEP_1_FA sample at $t=30$. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5% by w/w of cement)

Based on the H-B model, it was found that we need to incorporate at least 1% of sepiolite to improve the rheological parameters. Previously, nanoclays such as sepiolite, attapulgite, and montmorillonite are found to be promising alternative for reducing the formwork pressure by, increasing early age thixotropy and structural build-up. Using microscale sepiolite resulted with a less efficient impact. Such that generally a limited amount (0.3-0.5% by w/w cement) of nanoclays were found to be effective in terms of improving the rheological properties but herein we need at least 1% to see an improvement in rheological properties.

Increasing the particle size might reduce the filling affect of nano particles thus reducing the packing efficiency between cement particles. This will interfere with the formation of van der Waals forces which will reduce the degree of structural build up, thus the degree of thixotropy in the system compared to use of nano size clays like NM. To understand the effects of microscale sepiolite, further analysis was done to evalaute the rate of static yield stress evolution with time. Figure 4.19 demonstrates representative graphs for the static yield stress evolution for samples containing Sepiolite. Table 4.10 summarizes the average values and standard deviation obtained from triplicates of samples (See Appendix C for all other trials).

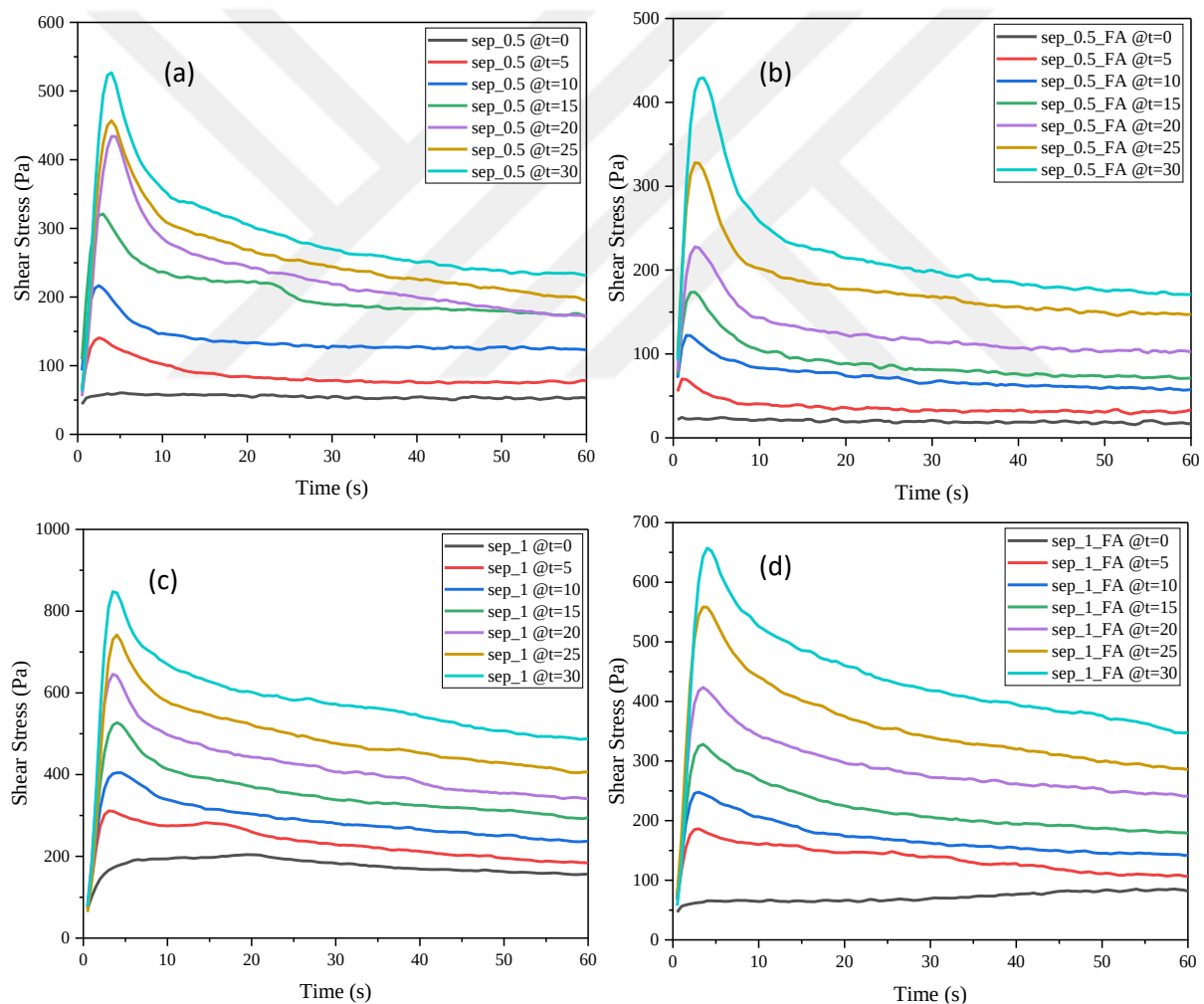


Figure 4.19: Shear stress (Pa) vs. time (s) graphs obtained at t=0,5,10,15,20,25,30 (a) shear profile for SEP_0.5 sample at different time intervals (b) shear profile for SEP_0.5_FA sample at different time intervals (c) shear profile for SEP_1 sample at different time intervals (d) shear profile for SEP_1_FA sample at different time intervals. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement)

Incorporation of sepiolite resulted with a considerable high rate of static yield stress evolution with time. Considering the micro scale particle size of sepiolite the impact was attributed to interaction of sepiolite entrapping water and acting like an internal fiber. Previously, Melo et al. [108] found that incorporation 1% low-CaO-sepiolite resulted with a higher rate of yield stress evolution compared to control samples as well as samples containing 2% sepiolite. In fact, 2% sepiolite exhibited a significantly higher yield stress right after mixing compared to 1% addition, but the rate of yield stress evolution was slower than that of it in 1% addition. Such behavior of sepiolite was explained by interlocking of fibrous structure and formation of gel-like crystalline on the particle surface, due to the dissolving calcium and hydroxyl ions of mineral when introduced to water. Wu and Kou [109] investigated the effects of high calcium sepiolite (>30% w/w) on rheological properties of cement-paste. The amount of sepiolite (<100 μ m) was held between 2.5 to 15% by weight of cement and the samples demonstrated an increasing viscosity and yield stress trend with increasing sepiolite dosage. As so, the increase in viscosity was more predominant compared to the increase in yield stress, particularly at lower dosages of sepiolite replacement (<5% w/w cement). There has been a very limited information regarding the influence of sepiolite on rheological performance of cement-based systems. Even with this limited information there are 3 critical points that should be considered for sepiolite (1) microscale sepiolite increases the yield stress and viscosity which might reduce the workability (2) the particle size is very important in order to improve the thixotropic behavior (3) the chemical composition of sepiolite is critical in terms of assessing structural build-up. Since the chemical composition of the sepiolite used in this study is rather unknown, it would be fair to evaluate the performance by establishing a comparison with the samples containing NM. Figure 4.20 and Table 4.11 summarizes the overall change in static yield stress with time and A_{thix} values for all samples tested in the study.

Table 4.10: The average static yield stress values obtained from static shear rate model at $t=0,10,20,30$ for mixtures containing SEP.

	time (min)	Average	
		Static τ_0	Std. Dev.
sep_0.5	0	56,4	3,9
	5	137,4	10,4
	10	215,9	9,9
	15	324,6	9,7
	20	403,0	65,1
	25	435,0	84,5
	30	477,5	56,5
sep_0.5_FA	0	25,5	1,5
	5	70,1	0,5
	10	128,8	10,7
	15	197,2	20,5
	20	238,9	12,3
	25	293,0	35,1
	30	373,1	57,4
sep_1	0	189,4	15,2
	5	317,5	25,0
	10	393,1	13,3
	15	492,2	33,4
	20	602,2	40,0
	25	698,8	51,0
	30	859,4	88,4
sep_1_FA	0	91,2	22,5
	5	232,0	48,0
	10	310,0	56,5
	15	408,6	69,8
	20	511,0	75,8
	25	649,8	79,7
	30	730,6	73,0

Table 4.11: A_{thix} values for all cement paste samples at different time intervals

Time at rest (min)	A_{thix} (Pa/s)											
	Control_SP	VMA_SP	SEP_0.5	SEP_1	NM_0.5	NM_1	Control_SP_FA	VMA_SP_FA	SEP_0.5_FA	SEP_1_FA	NM_0.5_FA	NM_1_FA
0-5	0,21	0,74	0,27	0,43	0,27	0,26	0,10	0,76	0,15	0,47	0,19	0,27
5-10	0,24	0,19	0,26	0,25	0,20	0,14	0,14	0,19	0,20	0,26	0,19	0,20
10-15	0,23	0,39	0,36	0,33	0,17	0,21	0,18	0,37	0,23	0,33	0,18	0,20
15-20	0,23	0,39	0,26	0,37	0,18	0,10	0,09	0,38	0,14	0,34	0,15	0,19
20-25	0,26	0,44	0,11	0,32	0,18	0,16	0,15	0,42	0,18	0,46	0,21	0,19
25-30	0,30	0,46	0,14	0,54	0,14	0,19	0,21	0,34	0,27	0,27	0,17	0,13

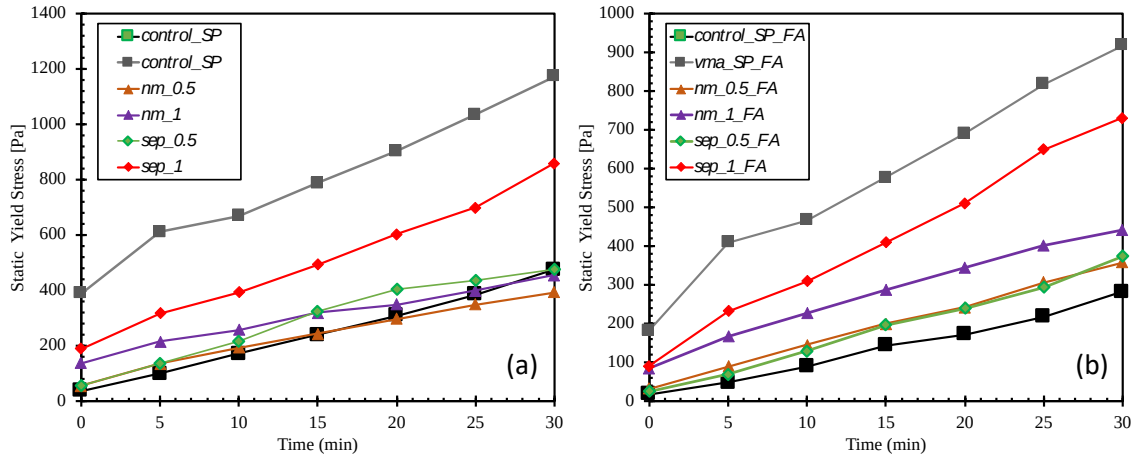


Figure 4.20: Comparative evaluation of static yield stress with time (a) without 20% fly ash (FA) replacement (b) with 20% fly ash (FA) replacement. Slope of each time interval reflect the A_{thix} coefficient.

Rheological analysis conducted on samples containin NM revealed that 1% NM addition was an optimum dosage to improve both static yield stress as well as the A_{thix} coefficient but impact of NM addition was only pronounced in FA amended samples. This was attributed to the lower thixotropic characteristics of the Control_SP_FA sample enabling NM induce a higher opposing charges and improving packing density resulting with a higher efficiency. A similar observation was also done for samples containin sepiolite. For both additives, 0.5% replacement was not sufficient to improve the structural build up. While 1% NM substitution provided a higher rate of static yield stress evolution only in NM_1_FA sample, 1% sepiolite replacement (SEP_1 and SEP_1_FA samples) resulted with a higher efficiency compared to all samples except their counterpart VMA samples. The higher efficiency of SEP compared to NM could be attributed to its additional interaction with the water phase. In general, montmorillonite is a swelling type of clay which enables its interaction with the water [110]. Surface modification on NM reduced its interaction with the water phase only leaving its affects due to surface attraction and fine particle size, thus most affecting the viscosity of the mix. Sepiolite increase flocculation and form a gel in presence of water which enables the mineral improve the stiffness of the paste at rest resulting with an increase in both yield stress and viscosity. However, neither

of these additives can actually provide a strong bridging effect like VMAs. VMAs are strong surfactants that are absorbed on cement particles and bridging the particles through steric hindrance while both NM and sepiolite can only trigger formation of weak van der Waals bonds. Incorporation of VMA results with a much stronger bonds, thus to a higher yield stress.

At last, a final evaluation for sepiolite containing samples were done structural recovery after a constant shear rate of 300s^{-1} . Figure 4.21 shows the results of 3-step evaluation done at 2 different shear rate. The sample was first subjected to a very low shear rate to simulate at rest conditions, loaded at high shear rates and then unloaded. The change in viscosity was recorded during this 3 step loading. As expected from the prior rheological analysis the structural recovery observed in SEP_0.5 and SEP_0.5_FA sample was slower than that of its counterpart NM samples. The SEP_0.5_FA sample took around 10 s to stabilize upon unloading. This was also observed in Control_SP_FA and VMA_SP_FA samples. However, increasing the sepiolite content 1% improved the structural build-up rate in the samples, particularly for SEP_1_FA sample.

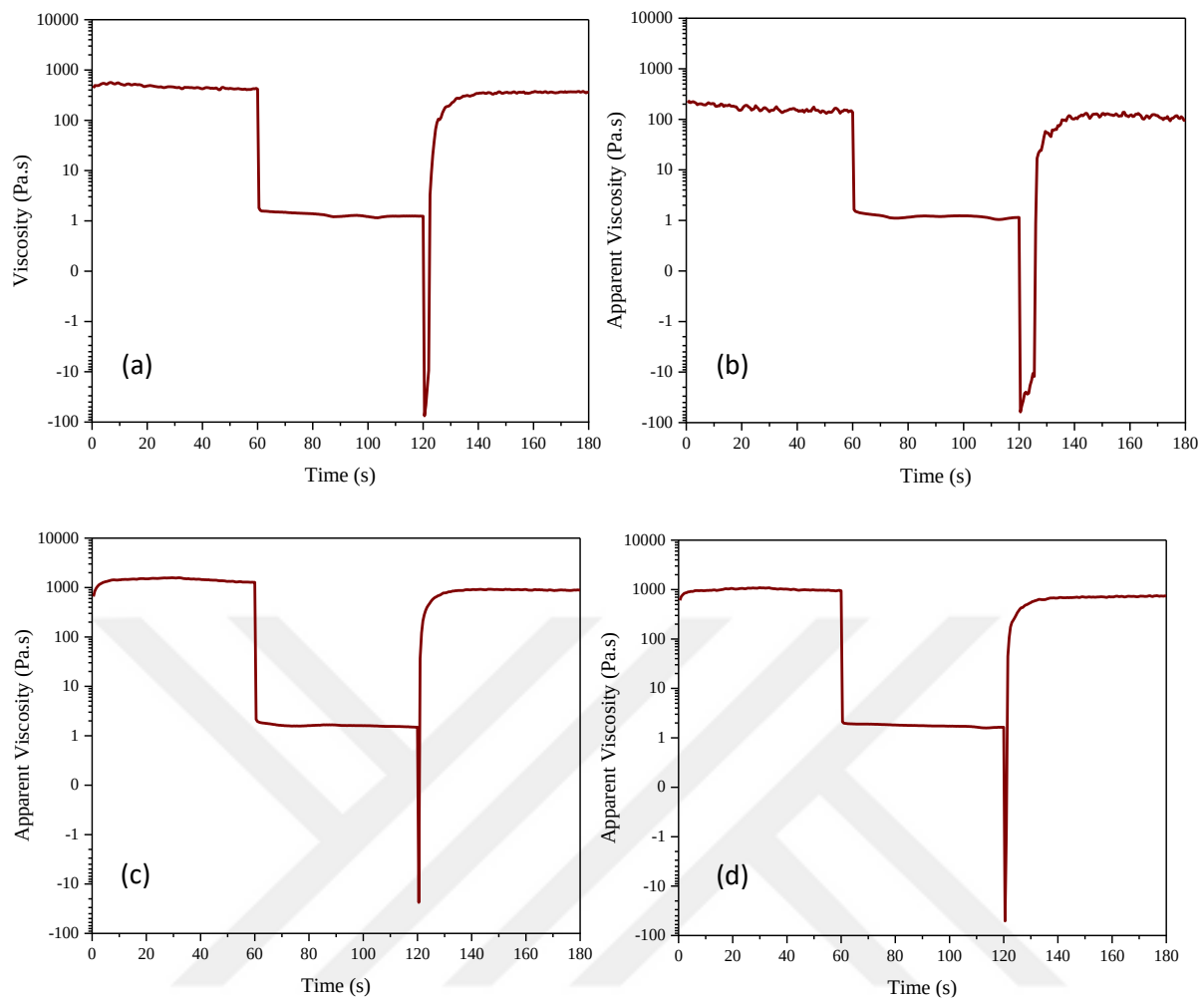


Figure 4.21: Effect of different shear rates on apparent viscosity of SEP containing samples. a) Apparent viscosity for SEP_0.5 sample (b) Apparent viscosity for SEP_0.5_FA sample (c) Apparent viscosity for SEP_1 sample (d) Apparent viscosity for SEP_1_FA sample. SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight; SEP: Sepiolite (0.5% and 1% by w/w of cement)

Table 4.12: Table 4.8: The comparative change in apparent viscosity before and after shear loading for cement paste samples, where Interval #1 describes the shearing period before shearing in 300s^{-1} and Interval #2 describes the shearing period after shearing in 300s^{-1}

	Apparent Viscosity values at constant shear [mPa.s]					
	control_SP	nm_0.5	nm_1	sep_0.5	sep_1	vma_SP
Interval #1	280,5	733,2	881,0	298,4	1223,3	2048,4
Interval #2	239,4	455,0	621,4	254,1	855,3	1567,1
%recovery	85%	62%	71%	85%	70%	77%
	control_SP_FA	nm_0.5_FA	nm_1_FA	sep_0.5_FA	sep_1_FA	vma_SP_FA
Interval #1	131,5	300,5	603,2	112,0	622,7	1617,5
Interval #2	103,3	226,4	442,4	81,1	536,2	1122,3
%recovery	79%	75%	73%	72%	86%	69%

4.4 Comparative evaluation of mini slump values

Besides the rheological analysis, a further evaluation was done by simple mini cone slump test to evaluate the workability of the mixes. Figure 4.22 summarizes the average mini slump cone diameters obtained from triplicates of samples. The results of the flow diameters were in line with the rheological measurements such that higher the static/dynamic yield stress indicated a lower flow diameter (Figure 4.23 a and b). Thus, it validates the argument that mini slump test could be correlated with the yield stress of the cement paste.

However, there is a complex relationship between % change in dynamic yield stress in 30 minutes to % change in flow diameter (Figure 4.23 c). Such that the higher the change in dynamic yield stress, the lower the % change in flow diameter. Interestingly, the highest increase in both dynamic yield stress within 30 minutes (directly was by only accounting for the difference between the measurements at $t=0$ and $t=30$) was recorded in control_SP sample while the sample exhibited a lower % change in flow diameter. But it should also be noted that, the change in these 2 parameters might exhibit a difference because of the difference in shear rates applied in these 2 tests. Even though, again not a direct relationship cannot be established between % change in flow and A_{thix} , it would be accurate to state that higher the A_{thix} value at 30 min, the lower the % change in flow. But it should be noted that the mini-slump cone test was conducted with a significantly lower shear rate, which was imposed to the self-weight of the sample. But the shear rate employed during the rheological analysis was much higher [99]. Considering the pseudo-plastic behaviour and increasing stiffness of cement paste with time, the material response to these two different shear modes would not be the same. Thus, it is more accurate to evaluate the time dependent change in the material through rheological analysis.

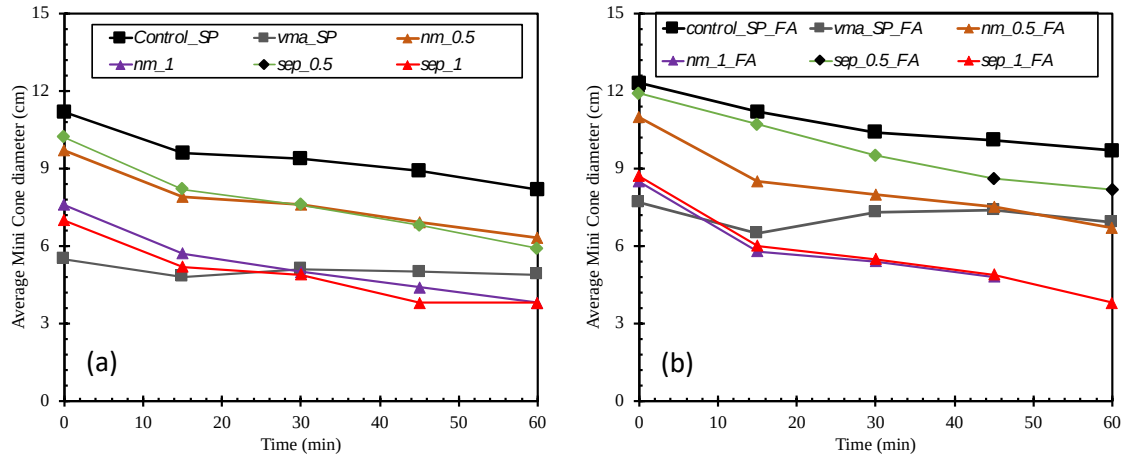


Figure: 4.22: Average mini cone diameters for all samples. SP: Superplasticizer (depends on the sample) FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement); NM: Nano montmorillonite (0.5 and 1% by w/w of cement); A 3.8 mm diameter indicates “0” slump

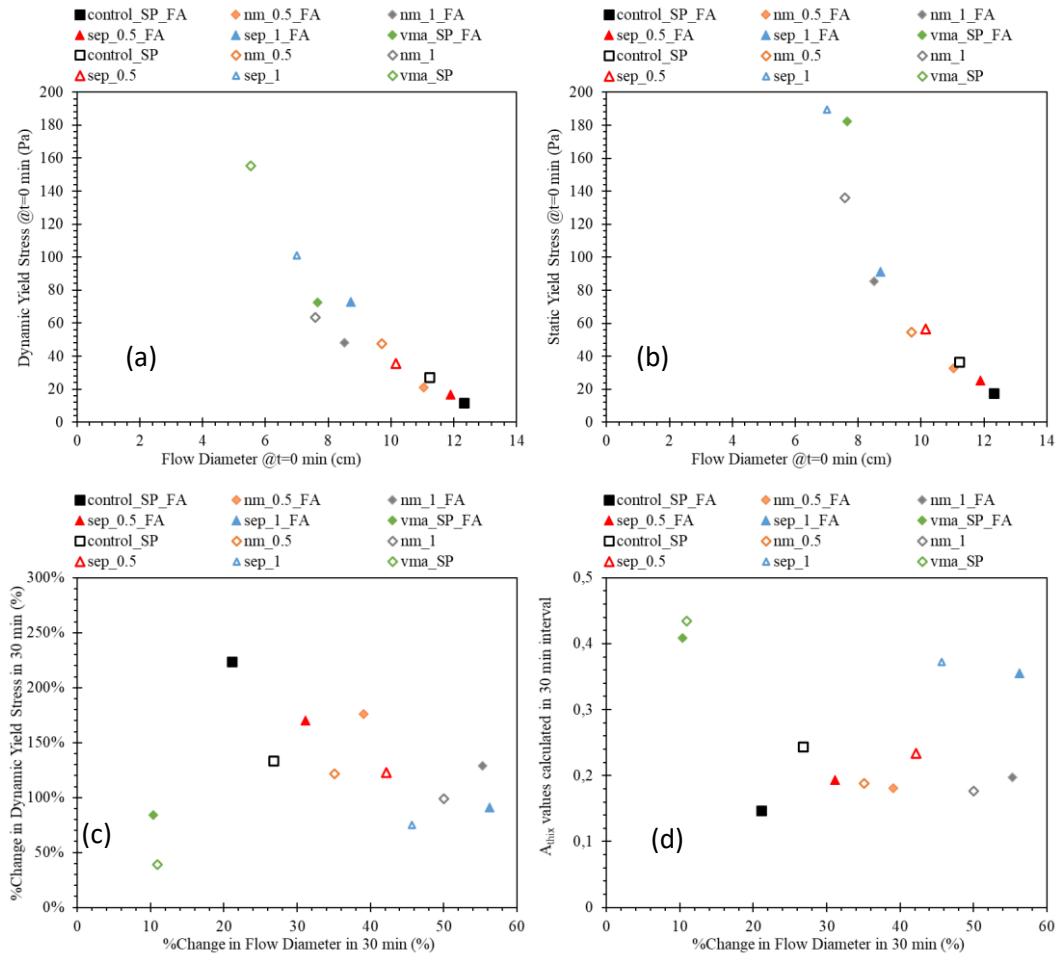


Figure: 4.23: Correlation of rheological parameters with flow diameter (a)dynamic yield stress vs flow diameter at t=0 (b) Static yield stress vs flow diameter at t=0 (c) % change in dynamic yield stress and flow diameter in 30 minutes (d) A_{thix} vs. flow diameter in 30 minutes SP: Superplasticizer (depends on the sample) FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement); NM: Nano montmorillonite (0.5 and 1% by w/w of cement)

4.5 Printability evaluation of selected mixes

Upon evaluating 12 different sets of samples including the control samples under 3 different rheological models, we have established a series of 3D printing applications for the selected material. Even though the structuration rates are important, the static yield stresses must be considered for buildability and the dynamic yield stresses must be considered for extrudability. Depending on the type of printing, there might be more than one suitable mix design. Herein we used a ram extruder that has a 10 L capacity (see Chapter 3). Figure 4. 24 represents the images obtained from this 3D printing trials. We have decided to use the samples containing FA since the effects both NM and sepiolite were more pronounced in FA amended samples. Also, spherical FA particles possessed a better workability which might induce a lubricant affect during the extrusion process.

Through the rheological analysis, we have analysed the dynamic yield stress of the cementitious systems, which will affect the extrudability. Then, the static yield stress evolution and thixotropy were evaluated to understand the buildability of the materials. At last, the structural recovery was quantified as a % recovery in viscosity upon unloading of high shear load. Table 4.13 summarizes the A_{thix} values and % viscosity recovery for the selected mixes.

Table 4.13: A_{thix} values and % viscosity recovery for the selected mixes. SP: Superplasticizer (depends on the sample) FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement); NM: Nano-montmorillonite (0.5 and 1% by w/w of cement)

Time Interval	A_{thix} (Pa/s)				
	vma_SP_FA	nm_0.5_FA	nm_1_FA	sep_0.5_FA	sep_1_FA
0-5	0,76	0,19	0,27	0,15	0,47
5-10	0,19	0,19	0,20	0,20	0,26
10-15	0,36	0,18	0,20	0,23	0,33
15-20	0,38	0,15	0,19	0,14	0,34
20-25	0,42	0,21	0,19	0,18	0,46
25-30	0,34	0,17	0,13	0,27	0,27
%recovery in apparent viscosity	75%	73%	72%	86%	69%

Our first attempt was with NM_0.5_FA mix having a low dynamic yield stress with a relatively average static yield stress (Figure 4.22-a). In addition, this sample has a high workability at $t=0$ and demonstrated a 30% decrease in mini slump diameter in 30 minutes. While the low dynamic yield stress provided an ease of extrusion, the low static yield stress resulted with a poor buildability such that the printed element has failed from elastic buckling even after 3rd layer (Figure 4.25).

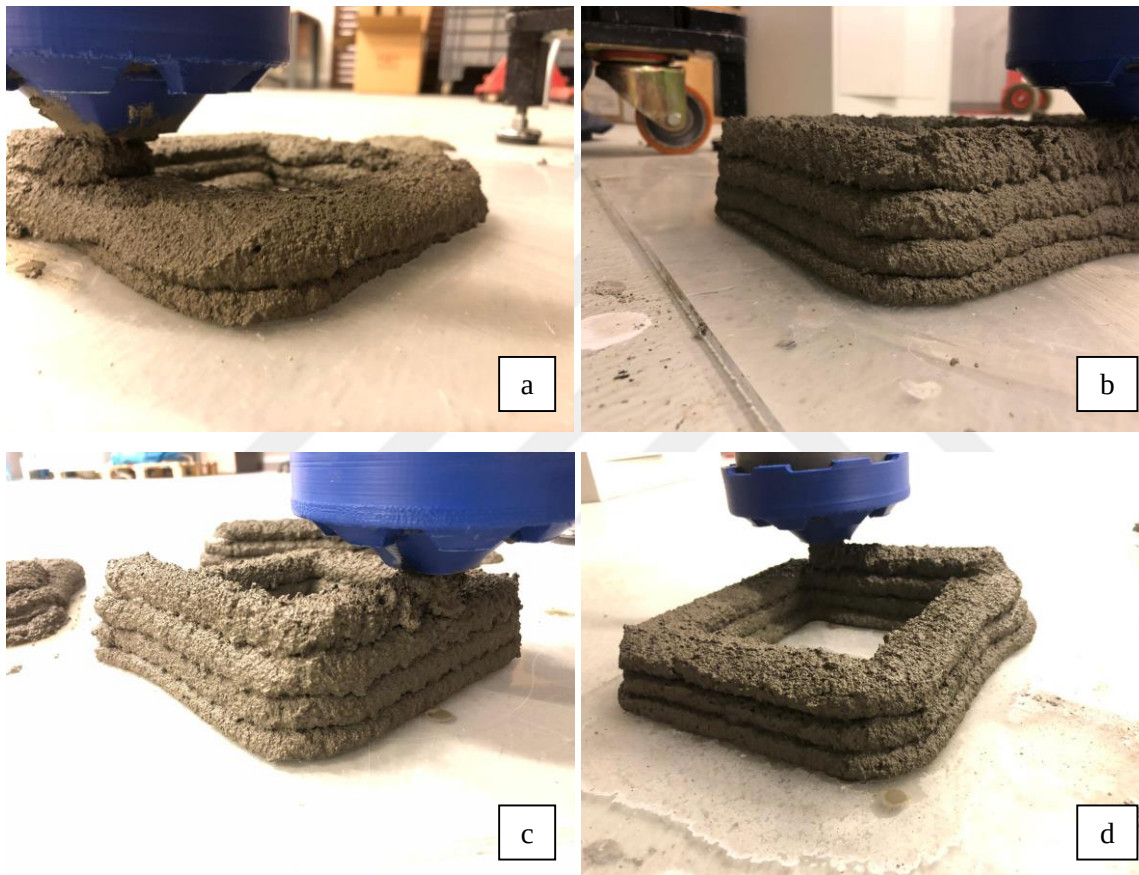


Figure 4.24: Preliminary printing trial images for (a) nm_0.5_FA, (b) nm_1_FA, (c) sep_0.5_FA and (d) vma_SP_FA. The images are taken while the printing was in progress. SP: Superplasticizer (depends on the sample) FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement); NM: Nano montmorillonite (0.5 and 1% by w/w of cement)



Figure 4.25: nm_0.5_FA sample after 15 minutes

Then we have printed a second set of trial with VMA_SP_FA which has very high static and dynamic yield stress with lower consistency index (Figure 4.25 d). While this mix exhibited an excellent buildability, its high dynamic yield stress created a stress on the printer during extrusion. The mix was stiff for a lab-scale printer and we needed to apply a higher torque to extrude the sample. Even though, the sample has a lower workability compared to Control_SP_FA samples, it almost possessed the same mini slump diameter for 60 minutes. Thus, this prevented the formation of cold joints. Based on these 2 trials, we actually obtained the 2 different ends of the printing evaluations. Figure 4.26 summarizes the relationship between static vs. dynamic yield stress as well as flow diameter vs. static yield stress.

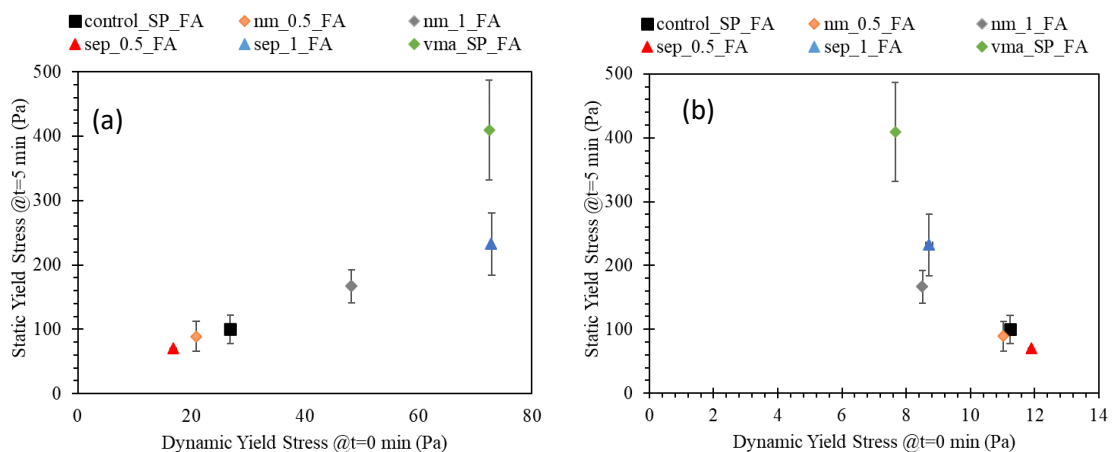


Figure 4.26: Correlation of parameters for selected mixes (a) static vs. dynamic yield stress (b) flow diameter vs. static yield stress SP: Superplasticizer (depends on the sample) FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement); NM: Nano montmorillonite (0.5 and 1% by w/w of cement)

The third trial was done with SEP_0.5_FA sample which exhibited similar behaviour on par with NM_0.5_FA (Figure 4.25c). The SEP_0.5_FA sample exhibited a similar static yield stress with a slightly higher dynamic yield stress. Interestingly, the mix possesses a better printability compared to NM_0.5_FA. This was mainly attributed to the fibrous microstructure provided a better interlocking during extrusion. Even though NM_0.5_FA exhibited a lower printability performance among all the samples tested, the sample might perform better if fibers added to the mix.

At last, but not the least, NM_1_FA mix performing a point in a range between VMA_SP_FA and NM_0.5_FA sample. SEP_0.5_FA sample exhibited the best performance in terms of structural recovery upon unloading in 3-step analysis with similar A_{thix} value compared to NM_0.5_FA. The sample provided ease of extrudability compared to VMA_SP_FA due to lower its lower dynamic yield stress. Even though, the static yield stress was less than VMA_SP_FA, it still provided the required buildability. This indicates that for a mix having static yield stress at $t=5$ min around 200 Pa would be sufficient to carry 4 layers of 15 mm. It should be noted that all printing process for 4 layers takes less than 3 minutes. The whole operation takes at most 10 minutes after mixing which corresponds to $t=5$ min in static evolution data considering the 5 min wait after pre-shear. NM_1_FA performed at most the best printing performance among all the samples tested with initial dynamic yield stress of 73 Pa and structural recovery of 72%. This indicates the minimum and threshold values for printable mixes adapted for ram extrusion (Figure 4.26). It should also be noted that SEP_1_FA had the highest structural recovery upon removal of shear rate, which showed that it might be the priori criteria to define the thixotropic behaviour required for 3D printing applications. The results showed that, there are a lot of possibilities in the mix design that enable us print concrete for the targeted structure. The flow behaviour of the concrete could be simulated by applying different rheological shear input models for a targeted 3D printer design.

Further investigations will be done to optimize cement-bases systems fitting into the targeted rheological and workability parameters showed in Figure 4.26.

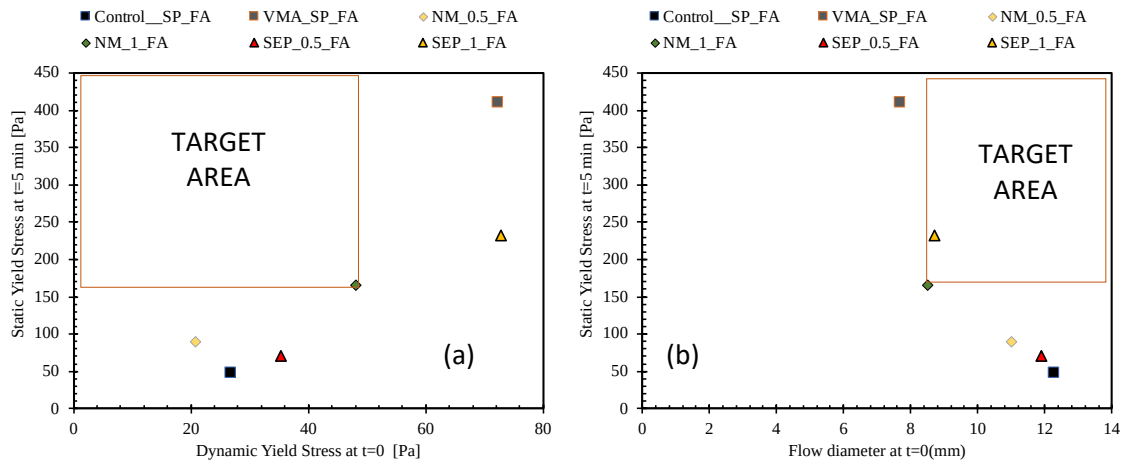


Figure 4.26: Target printability area defined by the trials (a) static vs. dynamic yield stress (b) flow diameter vs. static yield stress SP: Superplasticizer (depends on the sample) FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5 and 1% by w/w of cement); NM: Nano montmorillonite (0.5 and 1% by w/w of cement)

Chapter V

Conclusions

3D concrete printing technology has gained popularity with the 4th industrial revolution. The concrete printers are designed in a way that satisfy the needs of the digital construction. For printability, the fresh properties of traditional mix designs were found to be insufficient to meet with the printability requirements, such as extrudability, buildability, and interlayer bonding. The improvements in the Self Compacting Concrete field enabled the printability requirements to be understood and various researchers have developed mix designs.

The printability requirements have been investigated through fresh properties, such as static and dynamic yield stresses, dynamic and apparent viscosities, and thixotropy. For a concrete mix to be printable, it is found that the static yield stress gain would provide buildability, low dynamic stress would provide extrudability, viscosities would provide shape retention and thixotropy would provide buildability, thus change the interlayer bonding via changing the thixotropic open time (TOT).

The fresh properties of a printable concrete were studied via improved mix designs. In this sense, the PCE type superplasticizers, size of the aggregates, incorporation of pozzolans and incorporation of VMAs were found to be important. Besides the commercially available VMAs the clays were studied as viscosity modifiers. The interaction between clay-water, clay-cement and clay-SP enabled the printability requirements to be satisfied.

In this study, the rheological properties of 2 different types clays (NM and SEP) as viscosity modifiers were investigated with or without FA and compared by the rheological properties of control samples and commercially available starch ether VMA included mixtures. The rheology protocols were applied as if the printing process was simulated. Therefore, 3 different rheological input models were used: increasing shear rate model to simulate the extrusion process, static yield stress model to simulate the buildability and apparent viscosity model to simulate the viscosity recovery of the mixture after extrusion. The “Herschel and Bulkley” model was used to analyze the dynamic yield stress, consistency and decide whether the mixture is shear thinning or shear thickening, which gave insights of printability.

The results showed that:

- ✓ Printable mixtures require additional admixtures, such as VMA, as the properties of control samples did not allow printing.
- ✓ Incorporation of fly ash improved workability, however decreased the static yield stress of all types of mixes.
- ✓ FA incorporation in VMA, NM and SEP containing samples resulted in better rheological properties with respect to the control_SP_FA sample.
- ✓ Sudden decrease in the consistency index, K, was due to possible segregation.
- ✓ NM clay and SEP with 0.5% replacement had similar rheological results, however in preliminary printing trials SEP showed a better performance due to their structural differences.
- ✓ Thixotropic behaviour of VMA was independent of time, however in case of NM and SEP it was time dependent and they increased with respect to time clearly.
- ✓ Even though VMA incorporation increased the static and dynamic yield stresses, the %viscosity recovery was lower than the control samples.

Overall, the rheological parameters (dynamic and static yield stresses, hysteresis areas, structuration rate, mini cone flow diameters) were obtained by various experiments and the results were compared by the preliminary printing trials. The similar rheological properties of NM_0.5_FA and SEP_0.5_FA did not show the similar performances in preliminary printing trials due to structural differences. As the clay percentages were increased, the increase in the rheological performances were different from each other and SEP was found to be more effective when the amount was increased. Even though the clays have improved the rheological parameters, none of them showed the similar performance with the commercially available VMA. However, the printing performance was only compared by single printer and printing parameters. Therefore, the printing results would change when another printer is used. In terms of the best performance, the SEP containing mixtures had the best performance, which would be a possible printing material in cement-based mixtures. The rheological performance of the SEP_1_FA sample is an indication that it would have the best printing performance if it was possible to print that mixture.

Future Work

Even though the fibrous structure of SEP enabled better printing performance with respect to NM, the rheological enhancement in NM was higher. To be able to understand the reason of this enhancement, Nano-Sepiolite should be incorporated to make a better decision whether the size or reaction kinematics are the reason of this change, or fibres could be incorporated to the NM containing mixtures. XRD tests should be applied to understand the microstructural evolution. Bio-based VMA's would be used to compare additionally. As well as fresh properties, hardened properties such as interlayer bond strength, porosity, and compressive strengths should be experimented for structural purposes.

APPENDICES

Appendix A -- Shear Stress and Viscosity plots of all mixes

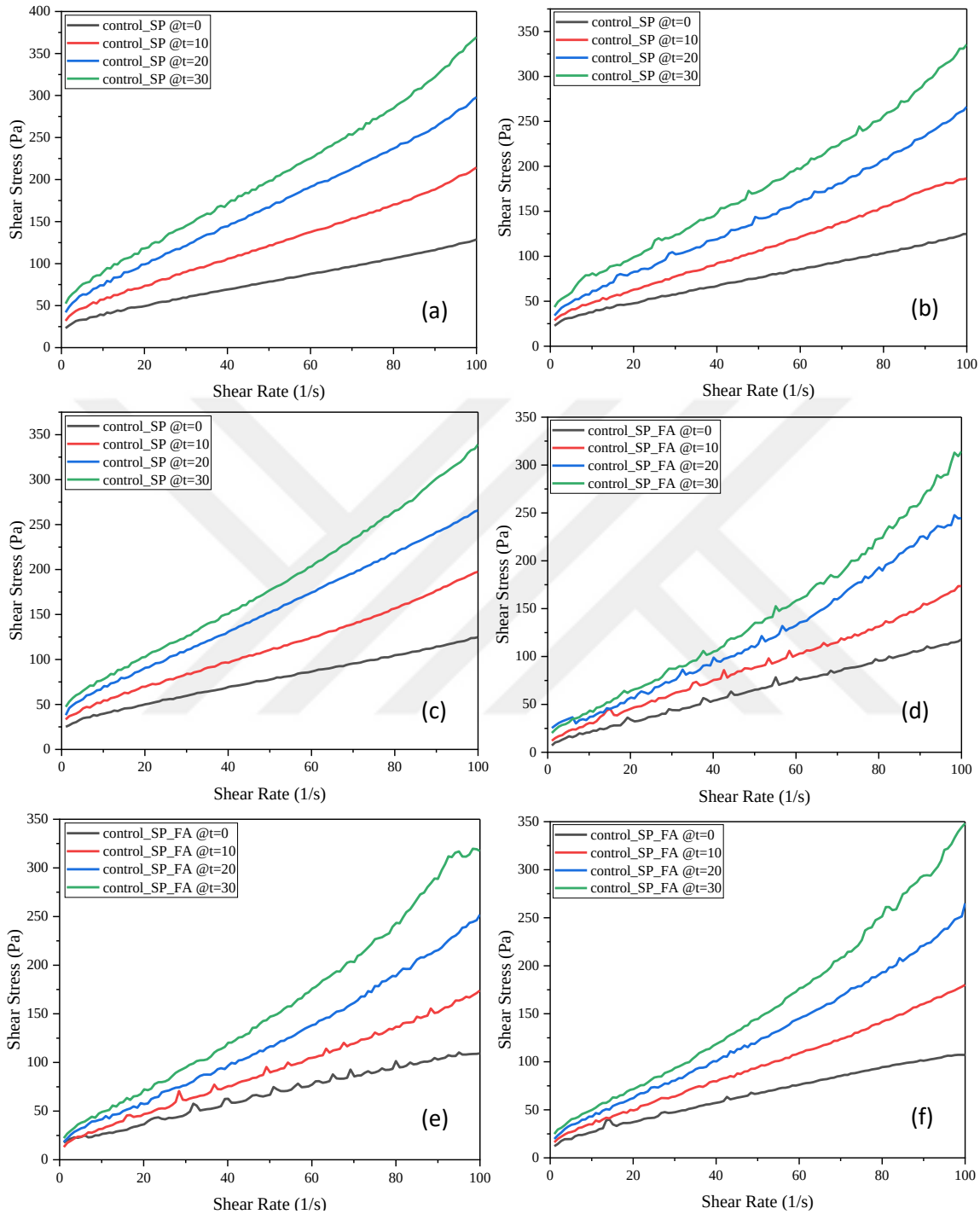


Figure A.1 Shear Profiles of control samples. (a) shear profile for control_SP sample at different time intervals (Trial 1) (b) shear profile for control_SP sample at different time intervals (Trial 2) (c) shear profile for control_SP sample at different time intervals (Trial 3) (d) shear profile for control_SP_FA sample at different time intervals (Trial 1). (e) shear profile for control_SP_FA sample at different time intervals (Trial 2) (f) shear profile for control_SP_FA sample at different time intervals (Trial 3). The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

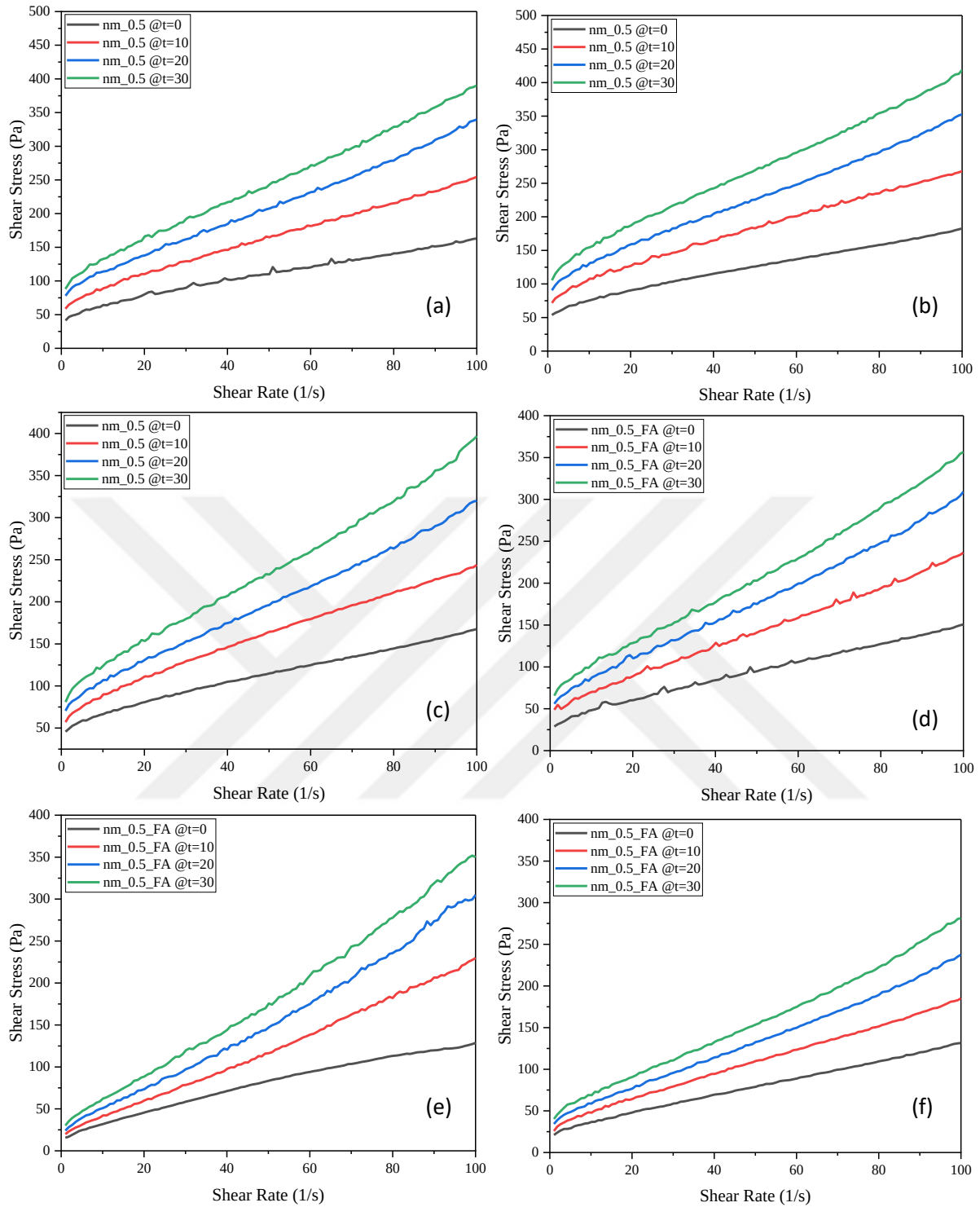


Figure A.2 Shear Profiles of samples containing Nano- montmorillonite (NM) (0.5% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) shear profile for NM_0.5 sample at different time intervals (Trial 1) (b) shear profile for NM_0.5 sample at different time intervals (Trial 2) (c) shear profile for NM_0.5 sample at different time intervals (Trial 3) (d) shear profile for NM_0.5_FA sample at different time intervals (Trial 1). (e) shear profile for NM_0.5_FA sample at different time intervals (Trial 2) (f) shear profile for NM_0.5_FA sample at different time intervals (Trial 3). The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

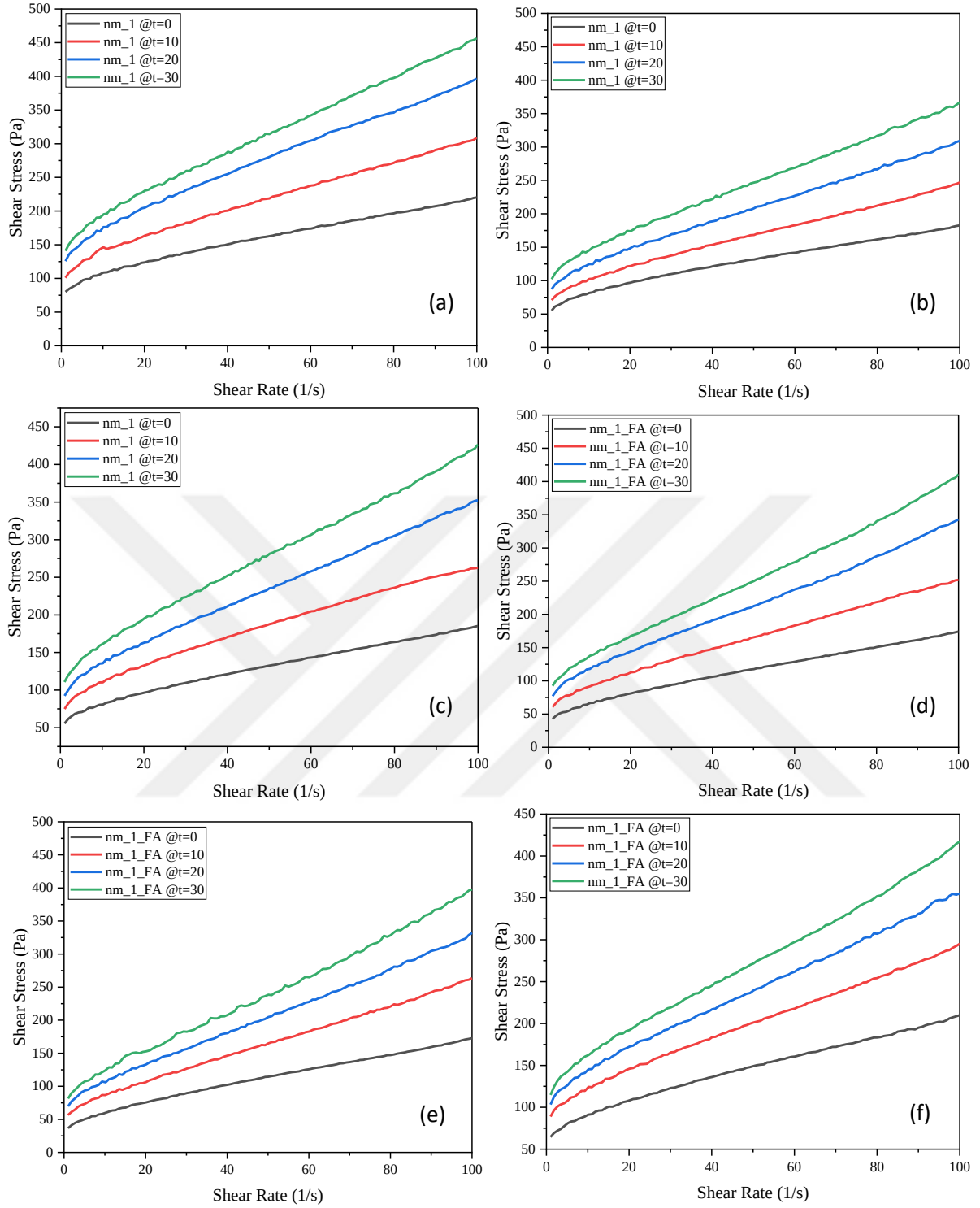


Figure A.3 Shear Profiles of samples containing Nano- montmorillonite (NM) (1% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) shear profile for NM_0.1 sample at different time intervals (Trial 1) (b) shear profile for NM_1 sample at different time intervals (Trial 2) (c) shear profile for NM_1 sample at different time intervals (Trial 3) (d) shear profile for NM_1_FA sample at different time intervals (Trial 1). (e) shear profile for NM_1_FA sample at different time intervals (Trial 2) (f) shear profile for NM_1_FA sample at different time intervals (Trial 3). The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

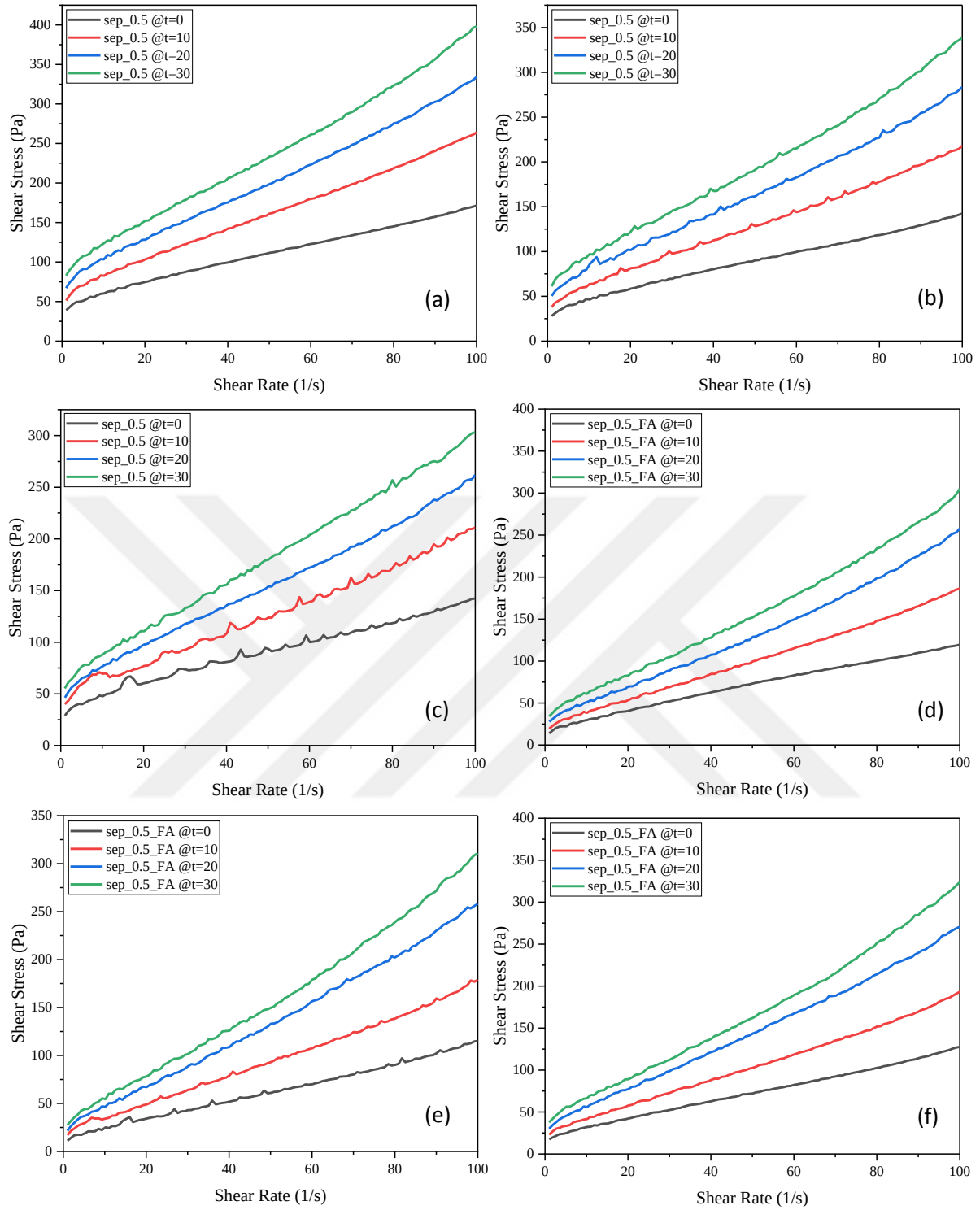


Figure A.4 Shear Profiles of samples containing sepiolite (SEP) (0.5% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) shear profile for SEP_0.5 sample at different time intervals (Trial 1) (b) shear profile for SEP_0.5 sample at different time intervals (Trial 2) (c) shear profile for SEP_0.5 sample at different time intervals (Trial 3) (d) shear profile for SEP_0.5_FA sample at different time intervals (Trial 1). (e) shear profile for SEP_0.5_FA sample at different time intervals (Trial 2) (f) shear profile for SEP_0.5_FA sample at different time intervals (Trial 3). The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

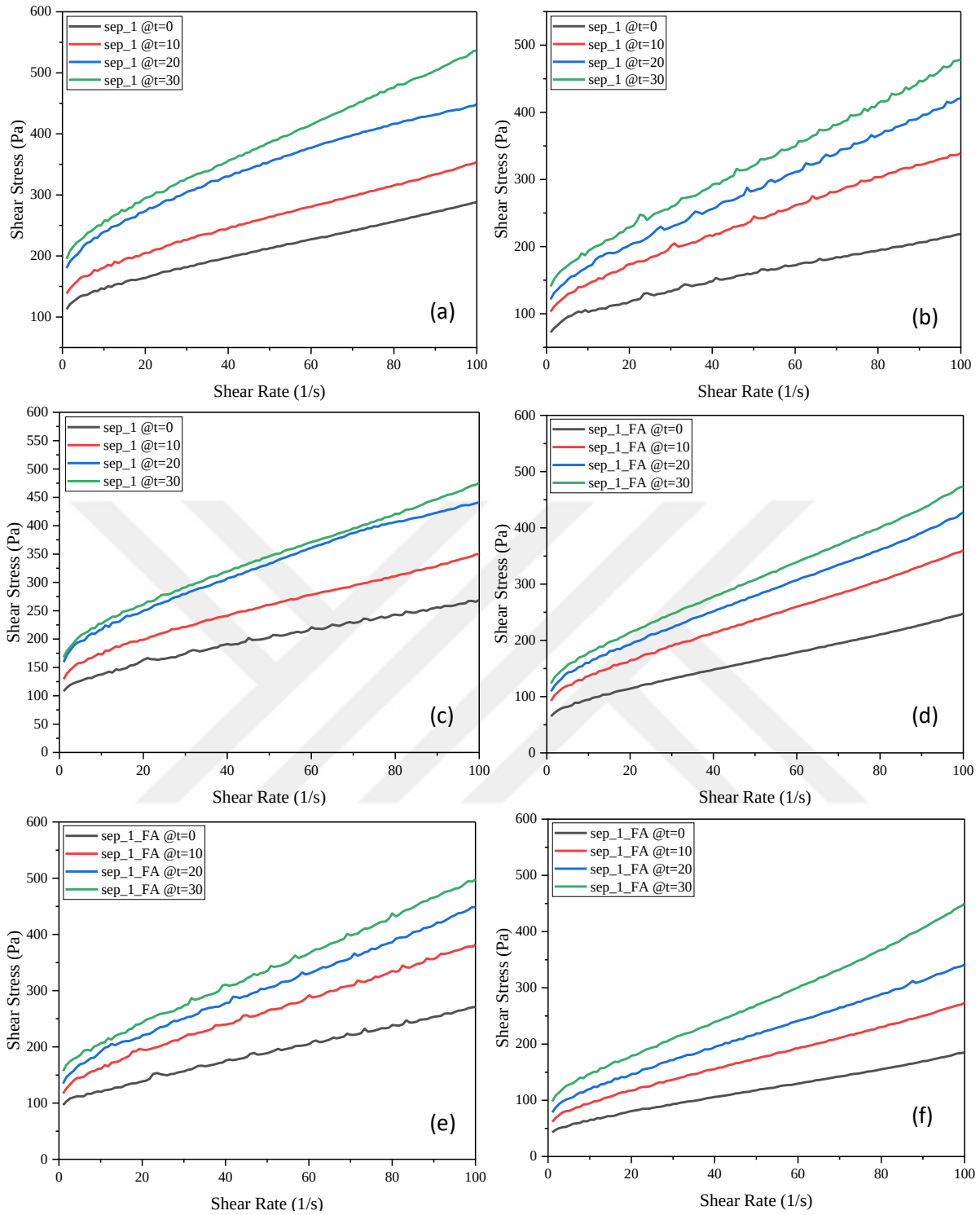


Figure A.5 Shear Profiles of samples containing sepiolite (SEP) (1% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) shear profile for SEP_1 sample at different time intervals (Trial 1) (b) shear profile for SEP_1 sample at different time intervals (Trial 2) (c) shear profile for SEP_1 sample at different time intervals (Trial 3) (d) shear profile for SEP_1_FA sample at different time intervals (Trial 1). (e) shear profile for SEP_1_FA sample at different time intervals (Trial 2) (f) shear profile for SEP_1_FA sample at different time intervals (Trial 3). The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

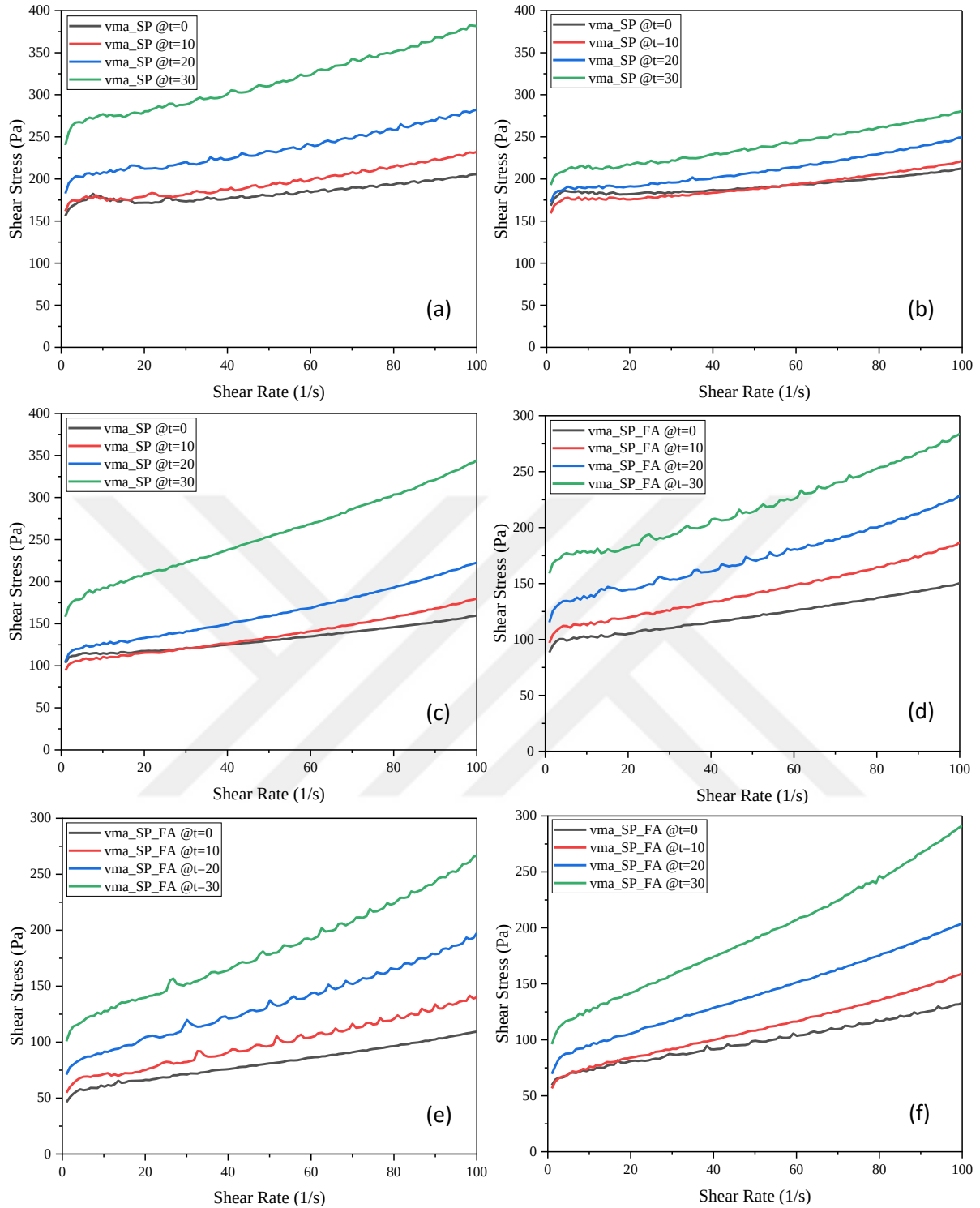


Figure A.6 Shear Profiles of samples containing viscosity modifying admixture (VMA) (0.3% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) shear profile for VMA_SP sample at different time intervals (Trial 1) (b) shear profile for VMA_SP sample at different time intervals (Trial 2) (c) shear profile for VMA_SP sample at different time intervals (Trial 3) (d) shear profile for VMA_SP_FA sample at different time intervals (Trial 1). (e) shear profile for VMA_SP_FA sample at different time intervals (Trial 2) (f) shear profile for VMA_SP_FA sample at different time intervals (Trial 3). The profile was analyzed by H-B model using the down-curve of the hysteresis loop. All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

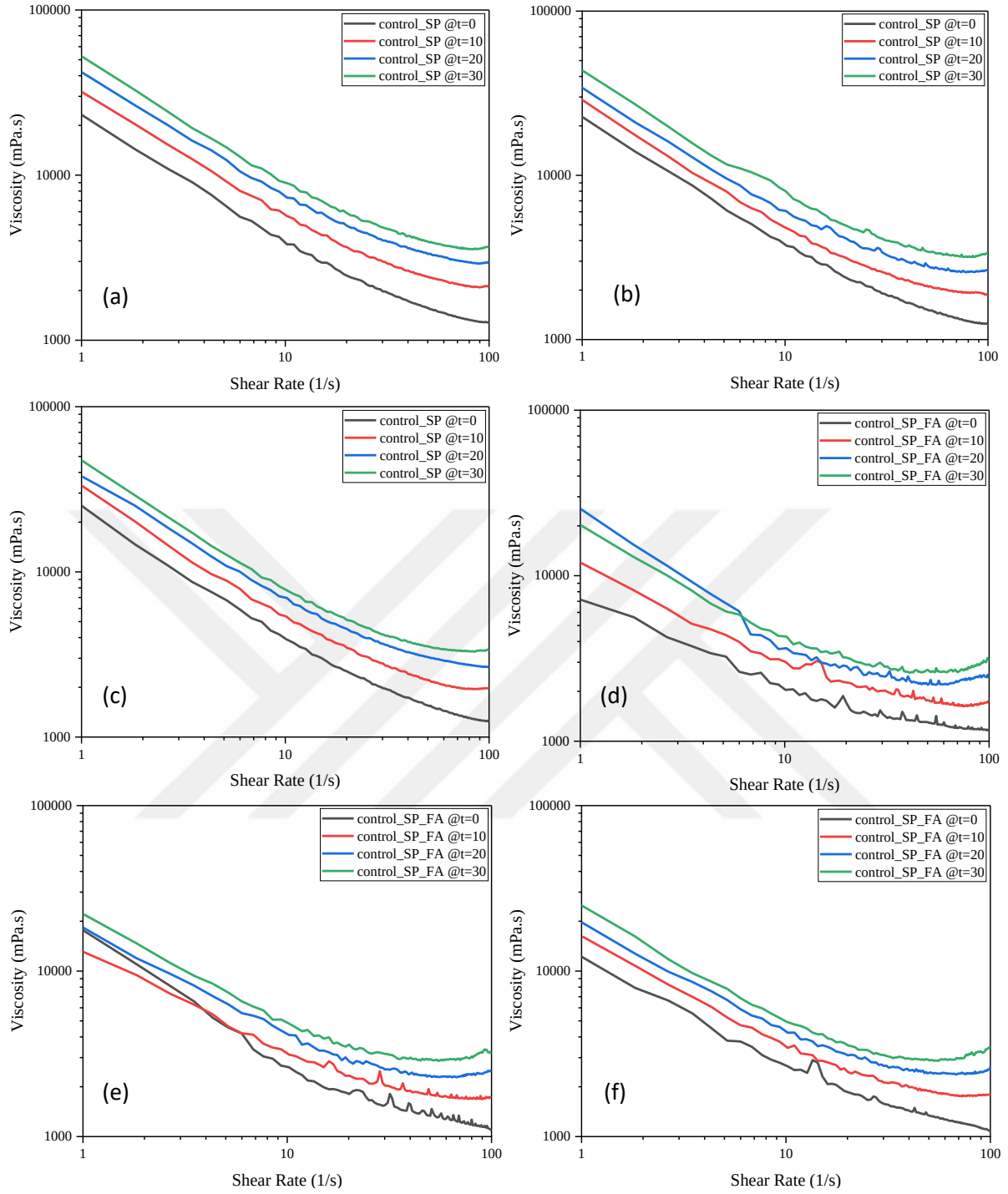


Figure A.7 Viscosity Profiles of control samples obtained from 3 trials of the increasing shear rate model. (a) viscosity profile for control_SP sample at different time intervals (Trial 1) (b) viscosity profile for control_SP sample at different time intervals (Trial 2) (c) viscosity profile for control_SP sample at different time intervals (Trial 3) (d) viscosity profile for control_SP_FA sample at different time intervals (Trial 1). (e) viscosity profile for control_SP_FA sample at different time intervals (Trial 2) (f) viscosity profile for control_SP_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

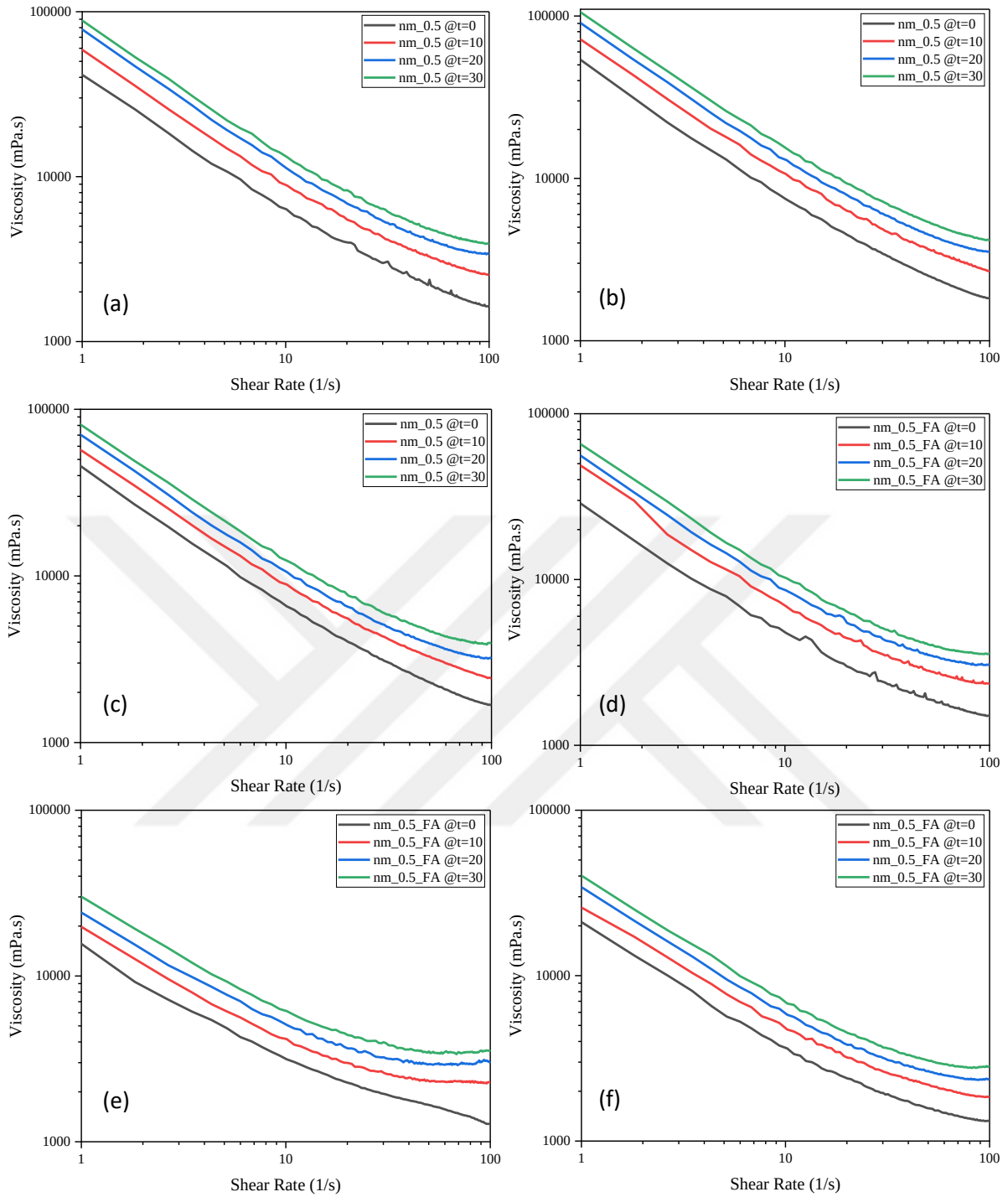


Figure A.8 Viscosity Profiles of samples containing Nano-montmorillonite (NM) (0.5% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) viscosity profile for NM_0.5 sample at different time intervals (Trial 1) (b) viscosity profile for NM_0.5 sample at different time intervals (Trial 2) (c) viscosity profile for NM_0.5 sample at different time intervals (Trial 3) (d) viscosity profile for NM_0.5_FA sample at different time intervals (Trial 1). (e) viscosity profile for NM_0.5_FA sample at different time intervals (Trial 2) (f) viscosity profile for NM_0.5_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

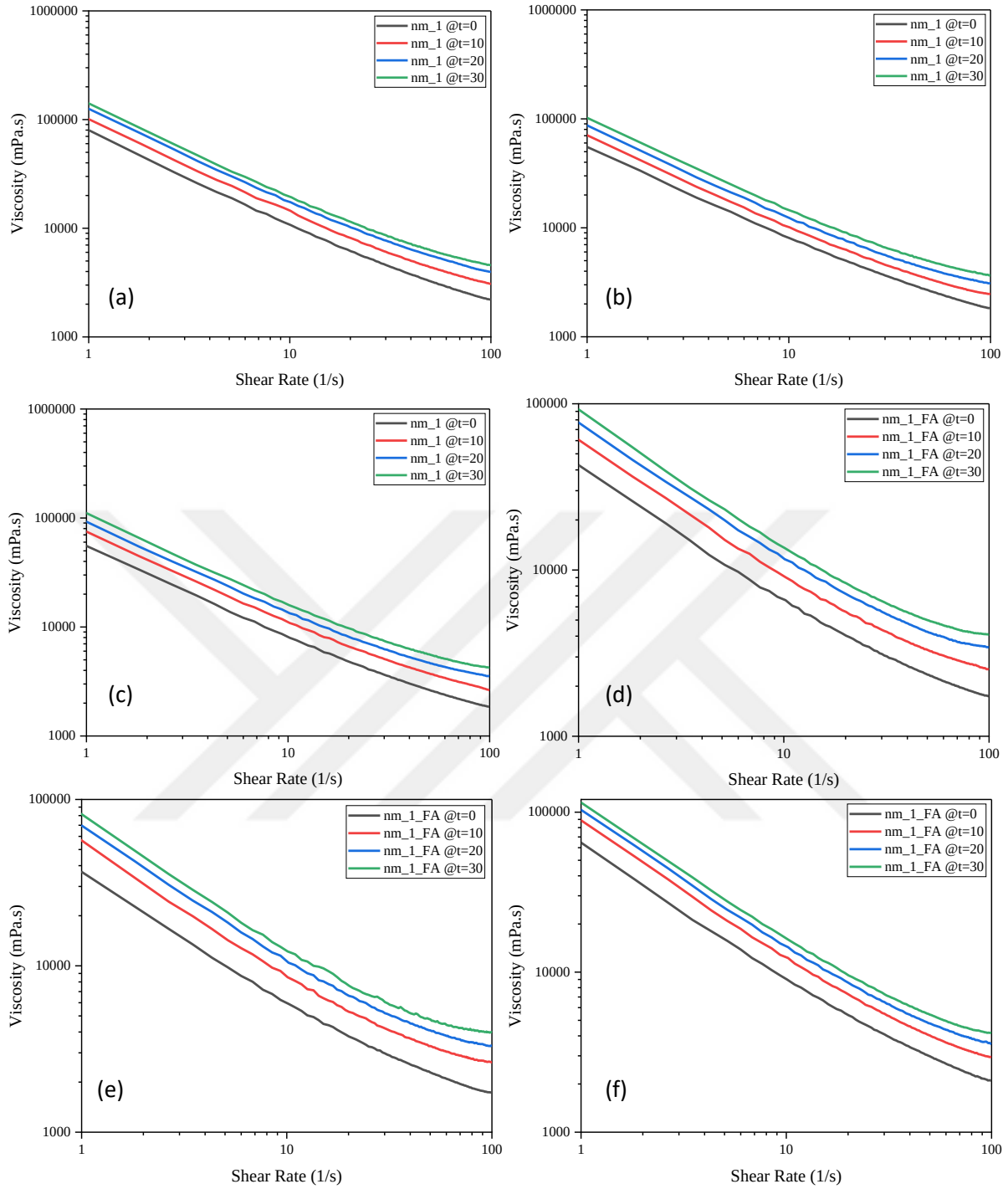


Figure A.9 Viscosity Profiles of samples containing Nano- montmorillonite (NM) (1% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) viscosity profile for NM_0.1 sample at different time intervals (Trial 1) (b) viscosity profile for NM_1 sample at different time intervals (Trial 2) (c) viscosity profile for NM_1 sample at different time intervals (Trial 3) (d) viscosity profile for NM_1_FA sample at different time intervals (Trial 1). (e) viscosity profile for NM_1_FA sample at different time intervals (Trial 2) (f) viscosity profile for NM_1_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

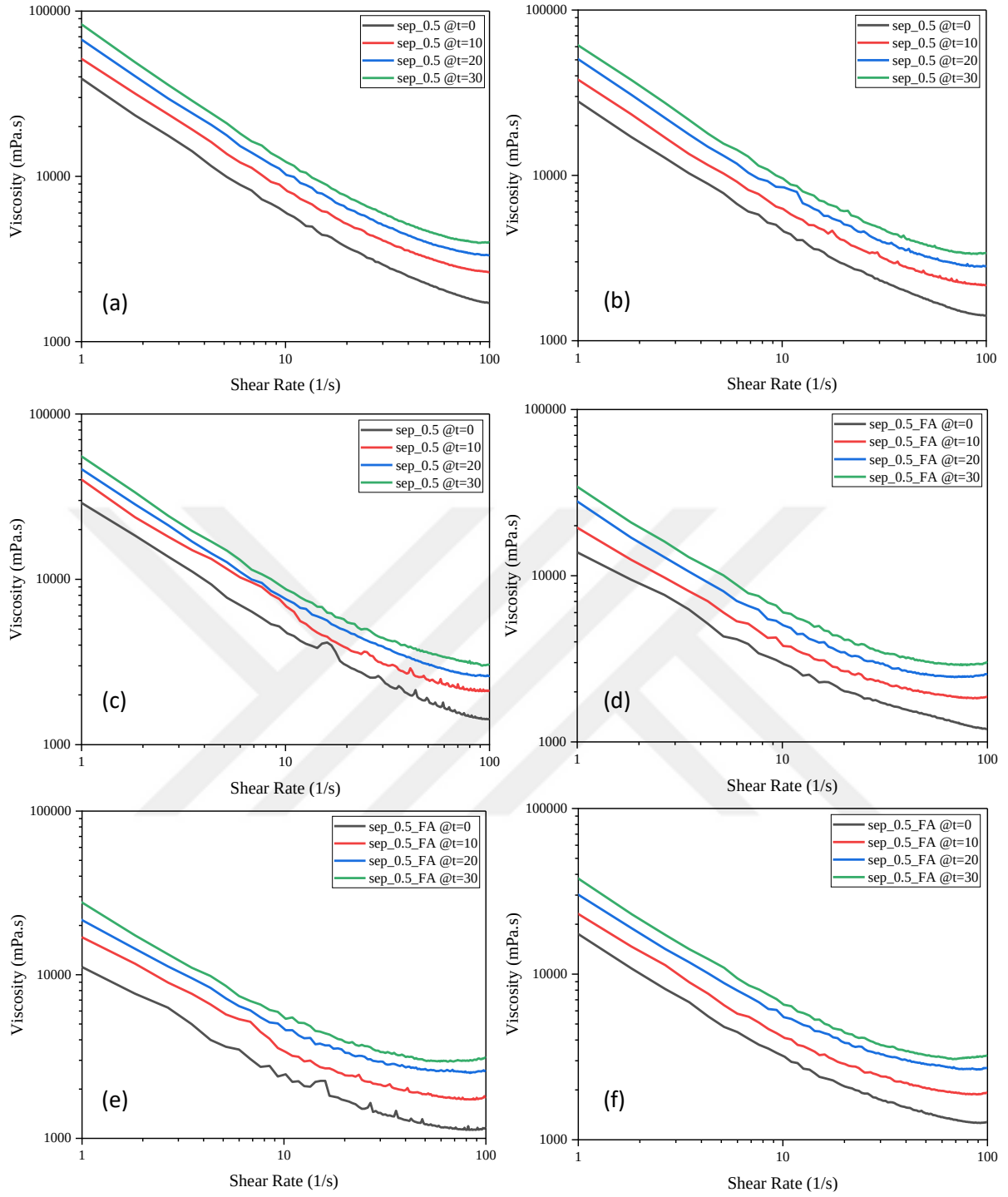


Figure A.10 Viscosity Profiles of samples containing sepiolite (SEP) (0.5% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) viscosity profile for SEP_0.5 sample at different time intervals (Trial 1) (b) viscosity profile for SEP_0.5 sample at different time intervals (Trial 2) (c) viscosity profile for SEP_0.5 sample at different time intervals (Trial 3) (d) viscosity profile for SEP_0.5_FA sample at different time intervals (Trial 1). (e) viscosity profile for SEP_0.5_FA sample at different time intervals (Trial 2) (f) viscosity profile for SEP_0.5_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

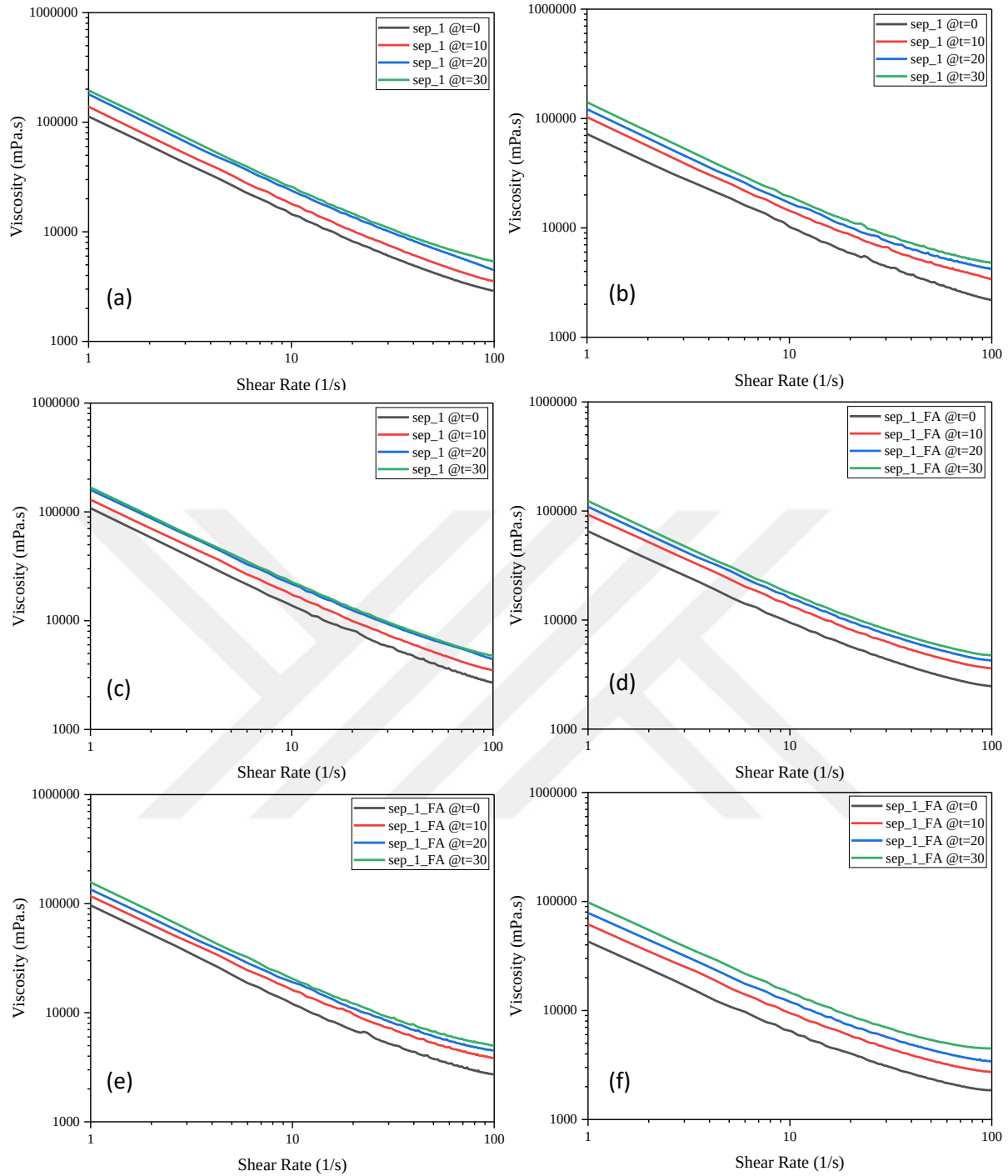


Figure A.11 Viscosity Profiles of samples containing sepiolite (SEP) (1% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) viscosity profile for SEP_1 sample at different time intervals (Trial 1) (b) viscosity profile for SEP_1 sample at different time intervals (Trial 2) (c) viscosity profile for SEP_1 sample at different time intervals (Trial 3) (d) viscosity profile for SEP_1_FA sample at different time intervals (Trial 1). (e) viscosity profile for SEP_1_FA sample at different time intervals (Trial 2) (f) viscosity profile for SEP_1_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

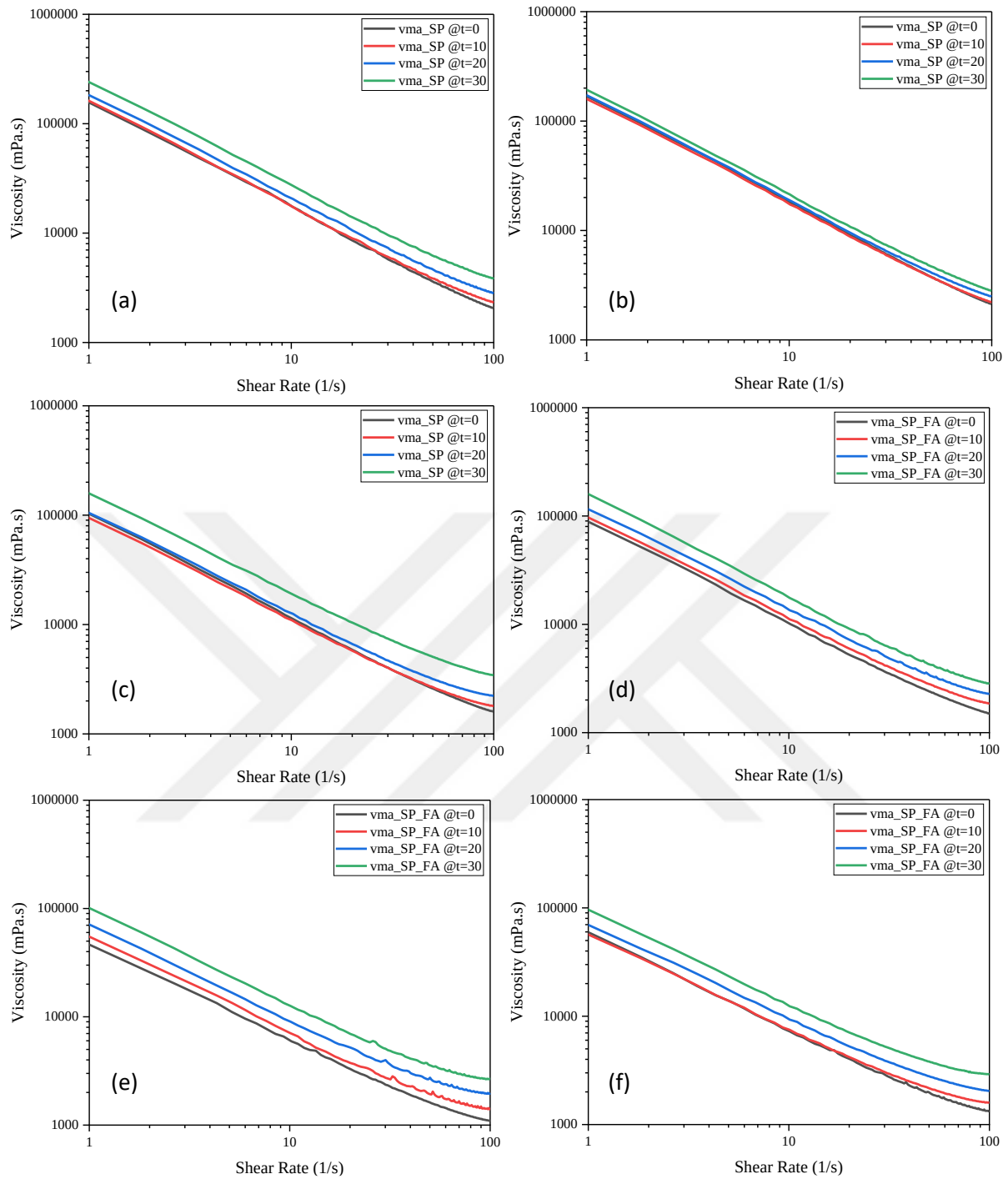
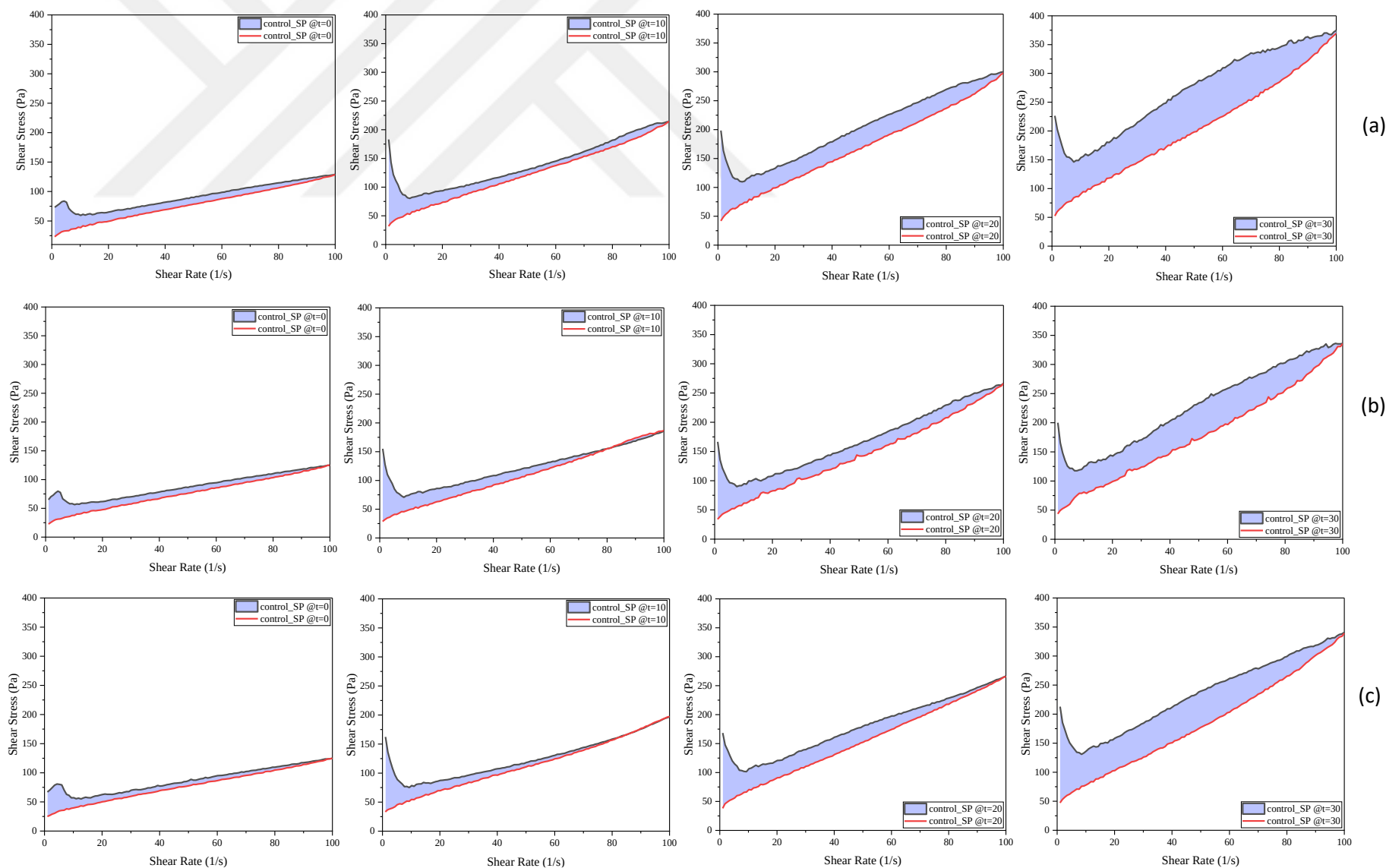


Figure A.12 Viscosity Profiles of samples containing viscosity modifying admixture (VMA) (0.3% by w/w of cement) obtained from 3 trials of the increasing shear rate model. (a) viscosity profile for VMA_SP sample at different time intervals (Trial 1) (b) viscosity profile for VMA_SP sample at different time intervals (Trial 2) (c) viscosity profile for VMA_SP sample at different time intervals (Trial 3) (d) viscosity profile for VMA_SP_FA sample at different time intervals (Trial 1). (e) viscosity profile for VMA_SP_FA sample at different time intervals (Trial 2) (f) viscosity profile for VMA_SP_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

Appendix B – Hysteresis Area plots of all mixes



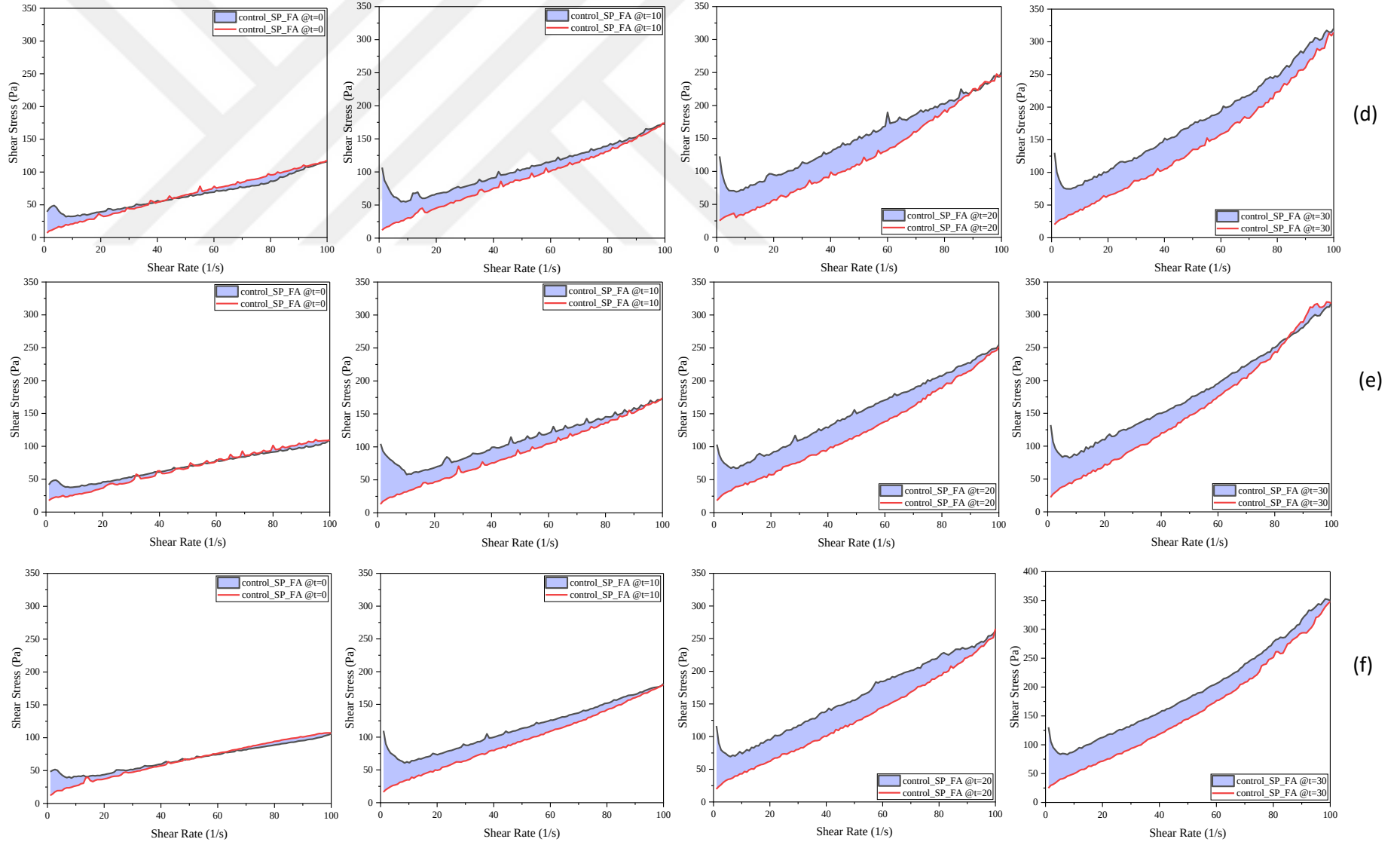
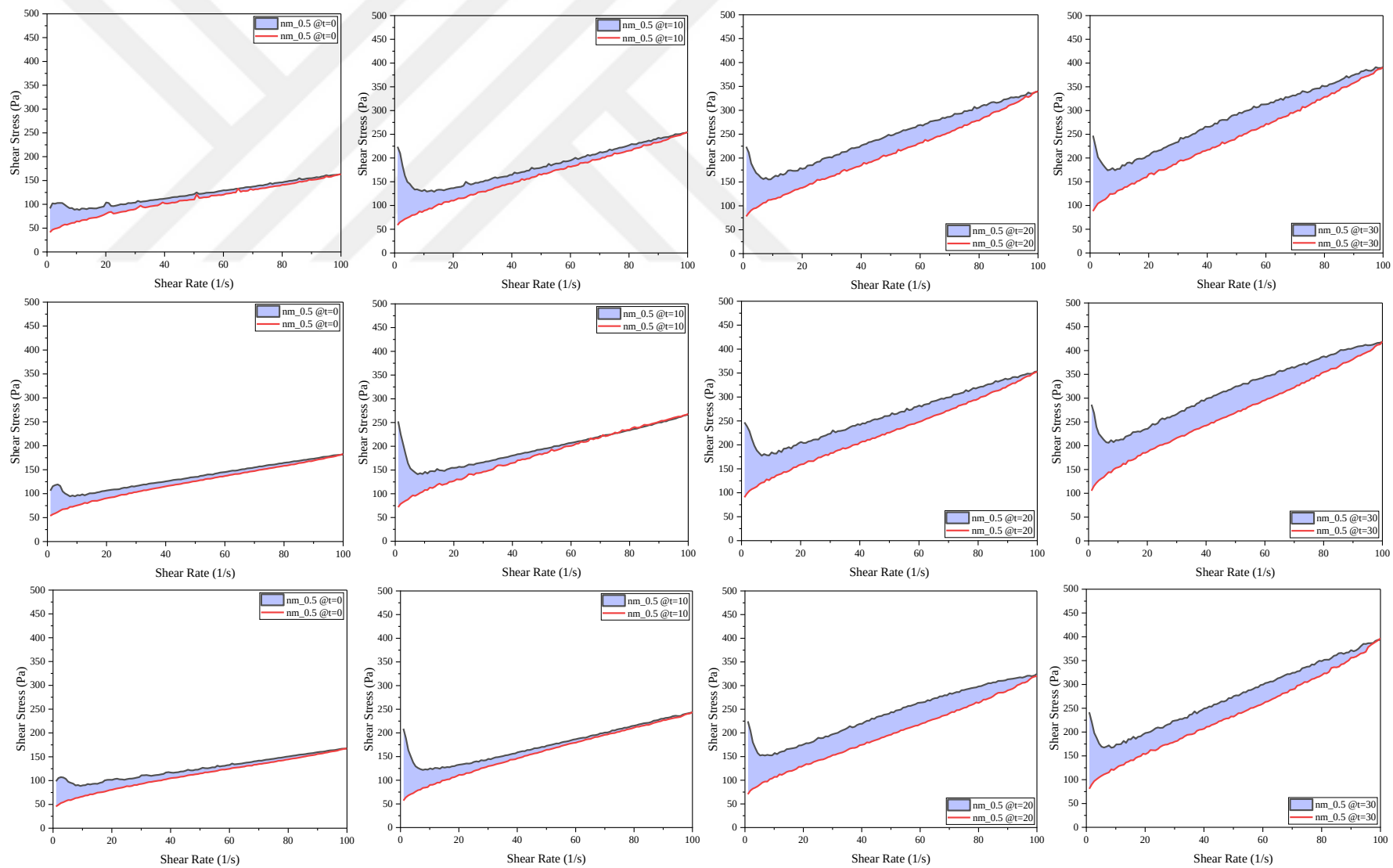


Figure B.1: Hysteresis areas for control mixtures obtained at all time intervals. The areas are between the up and down curves, shown in blue color. The plots are in order of increasing time (a) Hysteresis area for control_SP sample at all time intervals (Trial 1) (b) Hysteresis area for control_SP sample at all time intervals (Trial 2) (c) Hysteresis area for control_SP sample at all time intervals (Trial 3) (d) Hysteresis area for control_SP_FA sample at all time intervals (Trial 1) (e) Hysteresis area for control_SP_FA sample at all time intervals (Trial 2) (f) Hysteresis area for control_SP_FA sample at all time intervals (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)



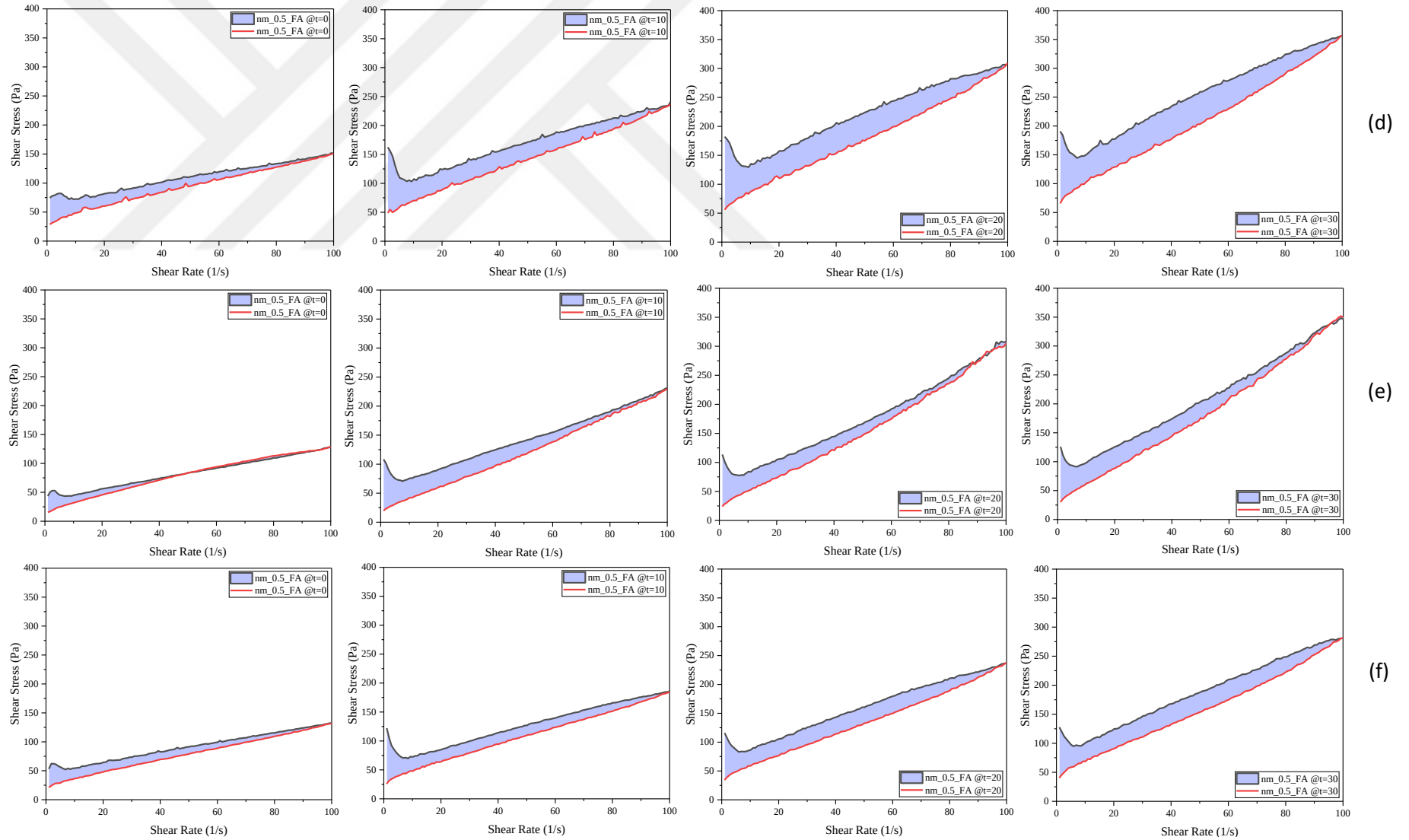
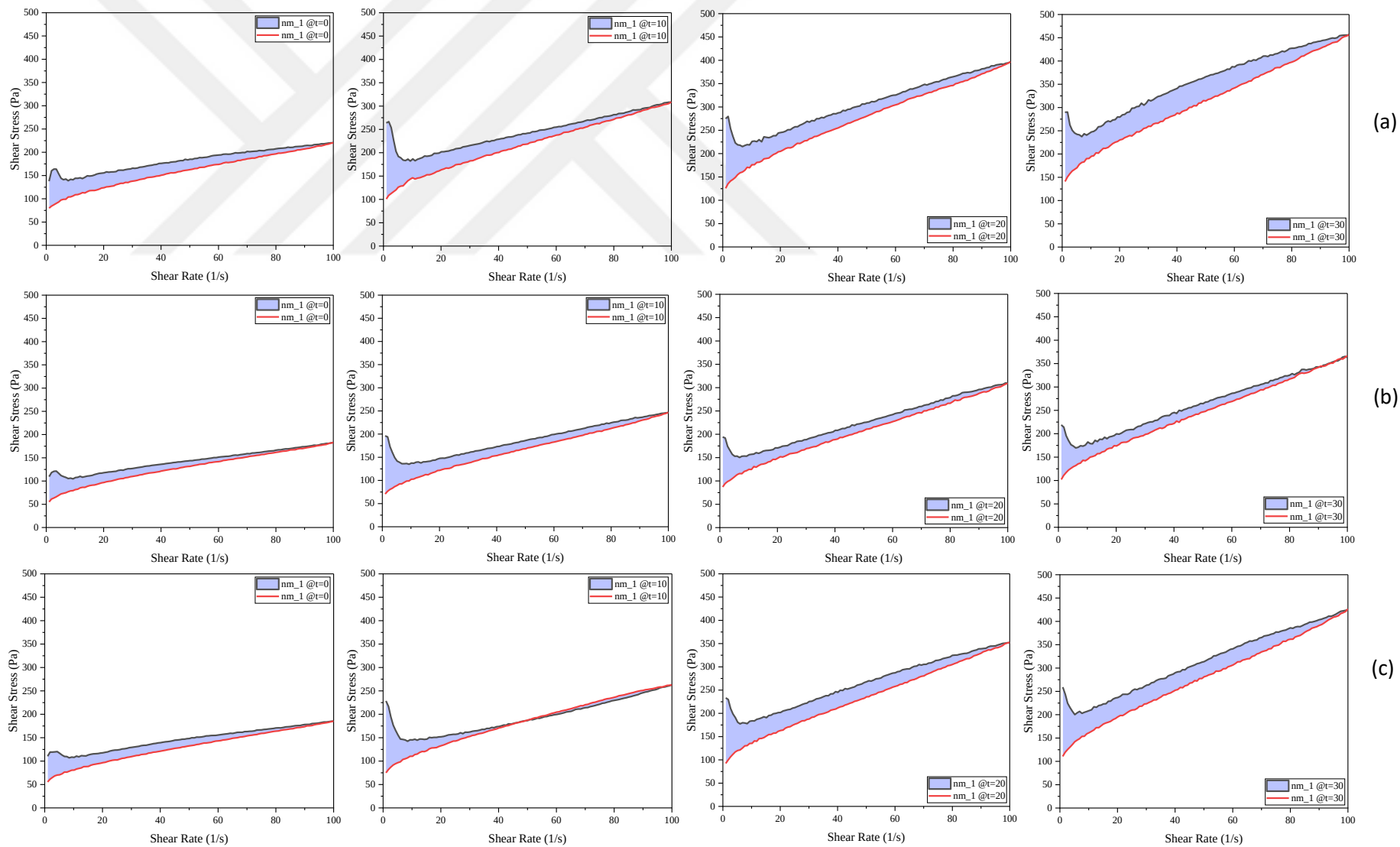


Figure B.2: Hysteresis areas for NM_0.5 and NM_0.5_FA mixtures obtained at all time intervals. The areas are between the up and down curves, shown in blue color. The plots are in order of increasing time (a) Hysteresis area NM_0.5 sample at all time intervals (Trial 1) (b) Hysteresis area for NM_0.5 sample at all time intervals (Trial 2) (c) Hysteresis area for NM_0.5 sample at all time intervals (Trial 3) (d) Hysteresis area for NM_0.5_FA sample at all time intervals (Trial 1) (e) Hysteresis area for NM_0.5_FA sample at all time intervals (Trial 2) (f) Hysteresis area for NM_0.5_FA sample at all time intervals (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (0.5% of w/w cement weight)



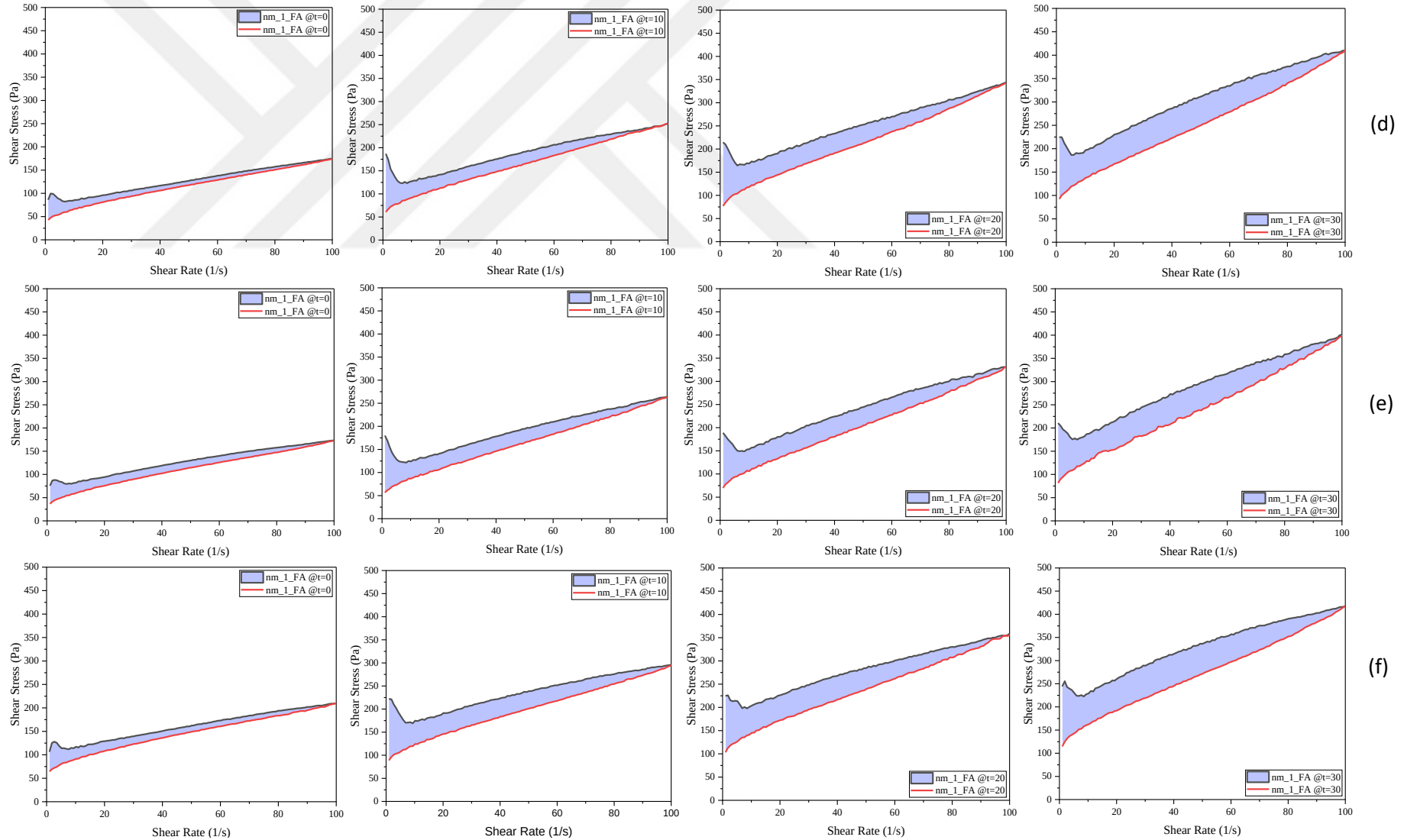
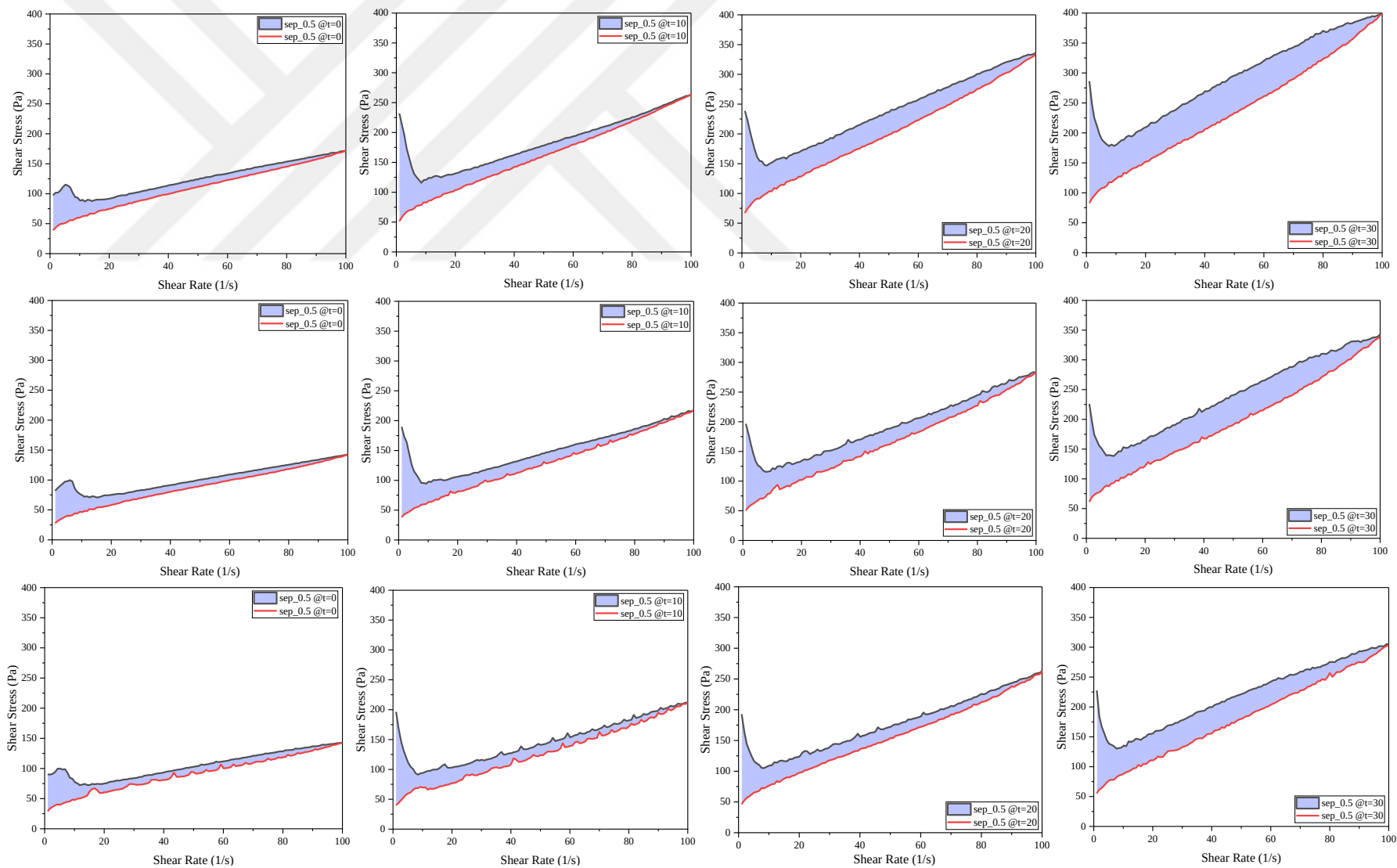


Figure B.3: Hysteresis areas for NM_1 and NM_1_FA mixtures obtained at all time intervals. The areas are between the up and down curves, shown in blue color. The plots are in order of increasing time (a) Hysteresis area NM_1 sample at all time intervals (Trial 1) (b) Hysteresis area for NM_1 sample at all time intervals (Trial 2) (c) Hysteresis area for NM_1 sample at all time intervals (Trial 3) (d) Hysteresis area for NM_1_FA sample at all time intervals (Trial 1) (e) Hysteresis area for NM_1_FA sample at all time intervals (Trial 2) (f) Hysteresis area for NM_1_FA sample at all time intervals (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (1% of w/w cement weight)



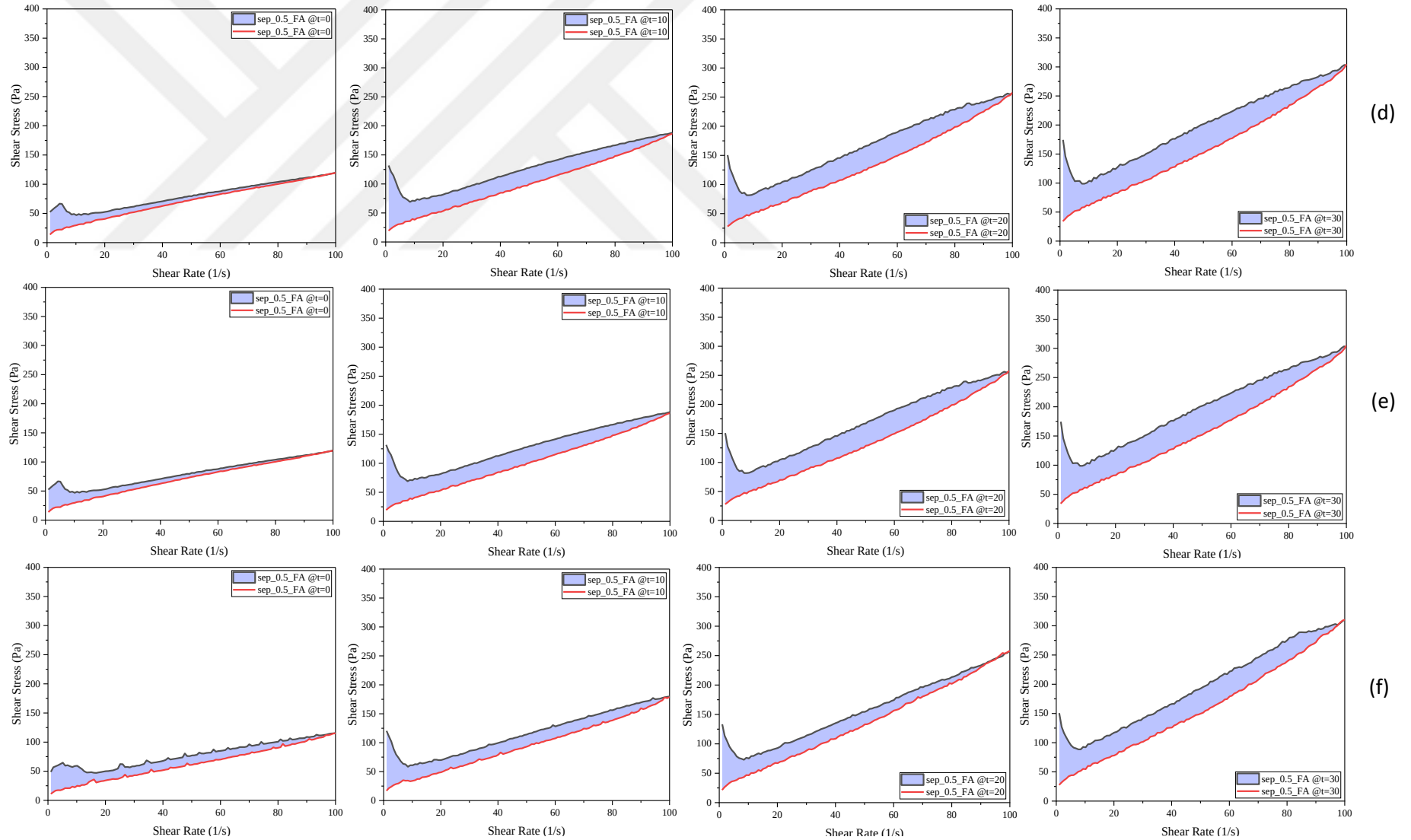
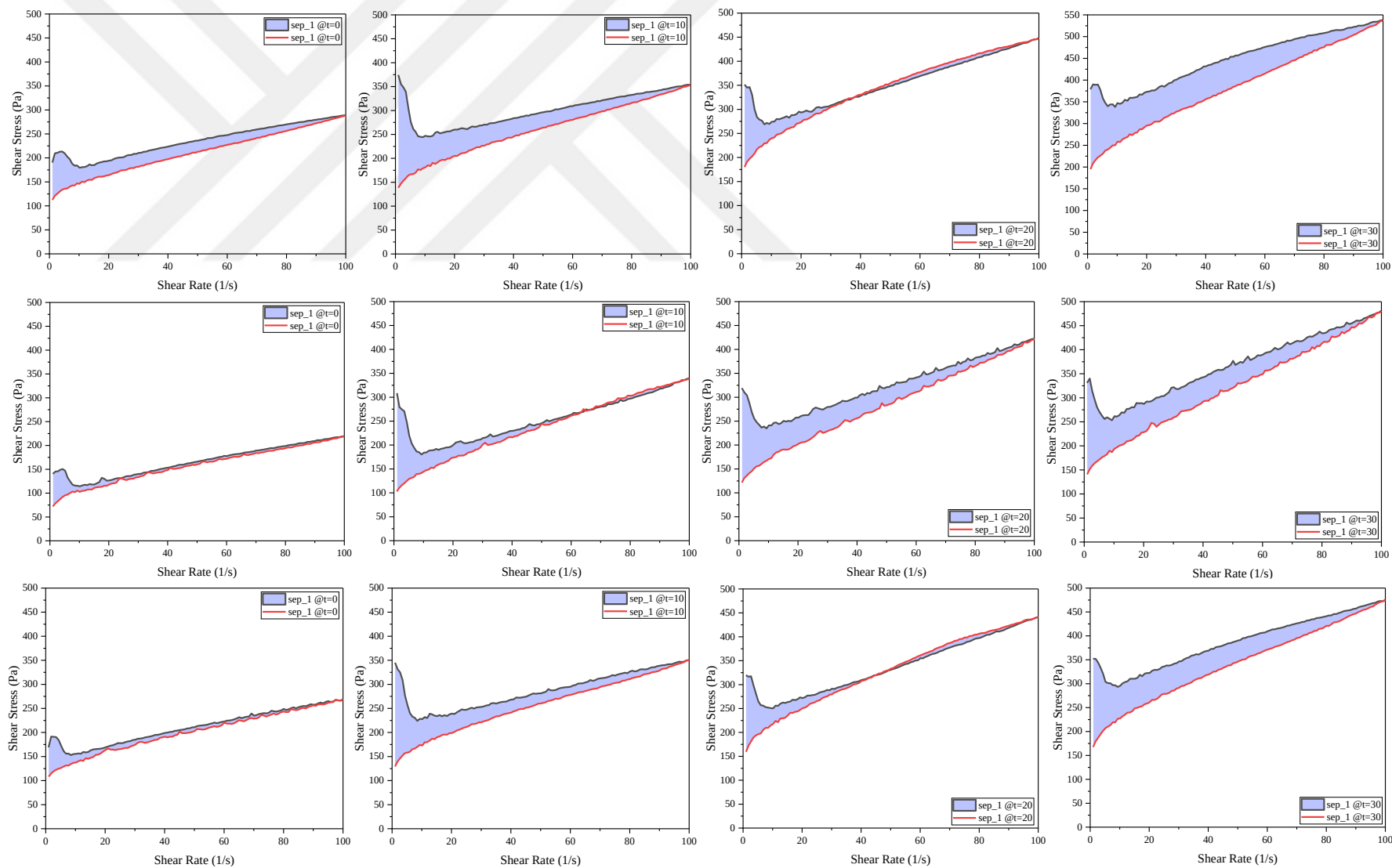


Figure B.4: Hysteresis areas for SEP_0.5 and SEP_0.5_FA mixtures obtained at all time intervals. The areas are between the up and down curves, shown in blue color. The plots are in order of increasing time (a) Hysteresis area SEP_0.5 sample at all time intervals (Trial 1) (b) Hysteresis area for SEP_0.5 sample at all time intervals (Trial 2) (c) Hysteresis area for SEP_0.5 sample at all time intervals (Trial 3) (d) Hysteresis area for SEP_0.5_FA sample at all time intervals (Trial 1) (e) Hysteresis area for SEP_0.5_FA sample at all time intervals (Trial 2) (f) Hysteresis area for SEP_0.5_FA sample at all time intervals (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5% of w/w cement weight)



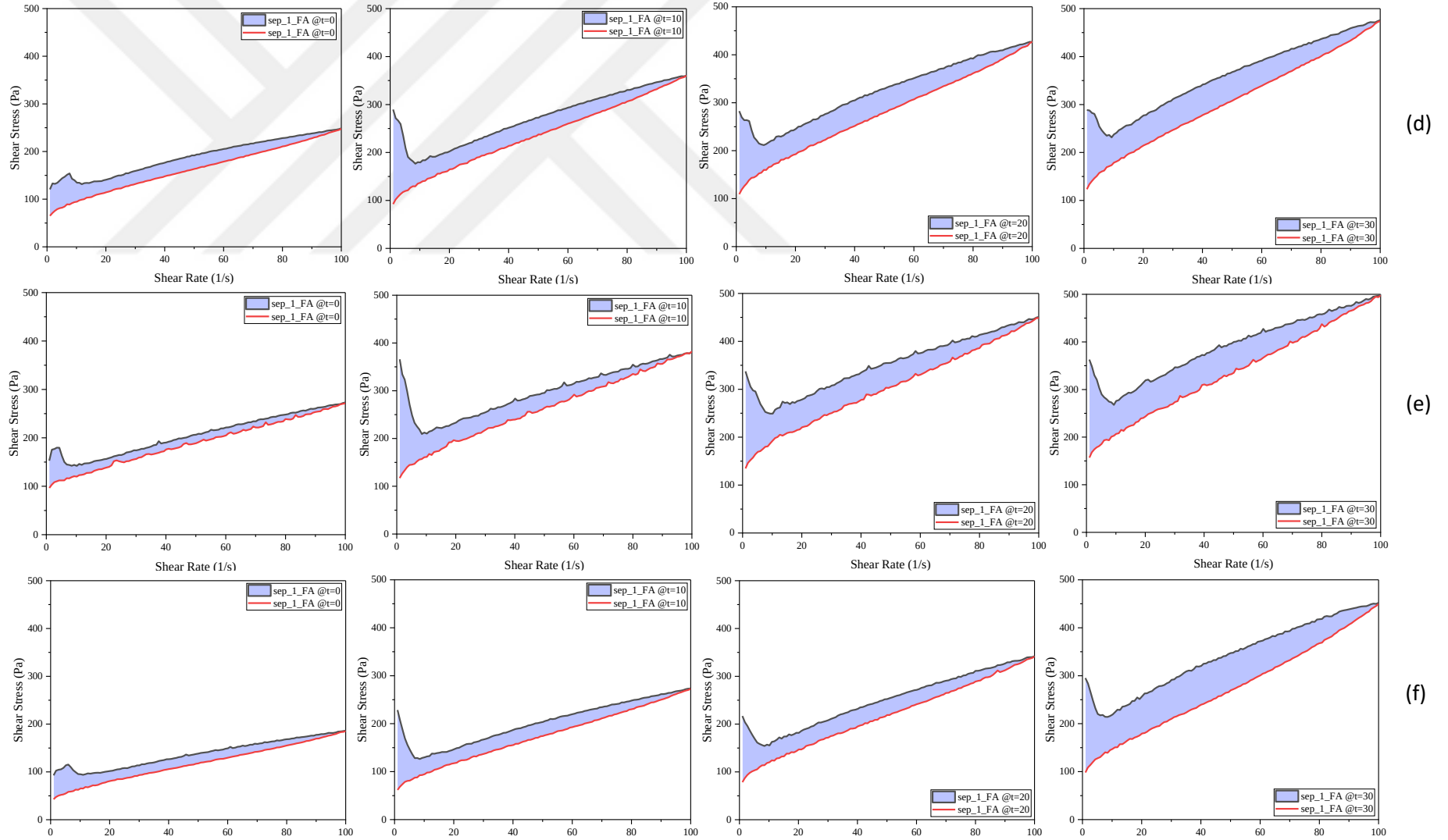
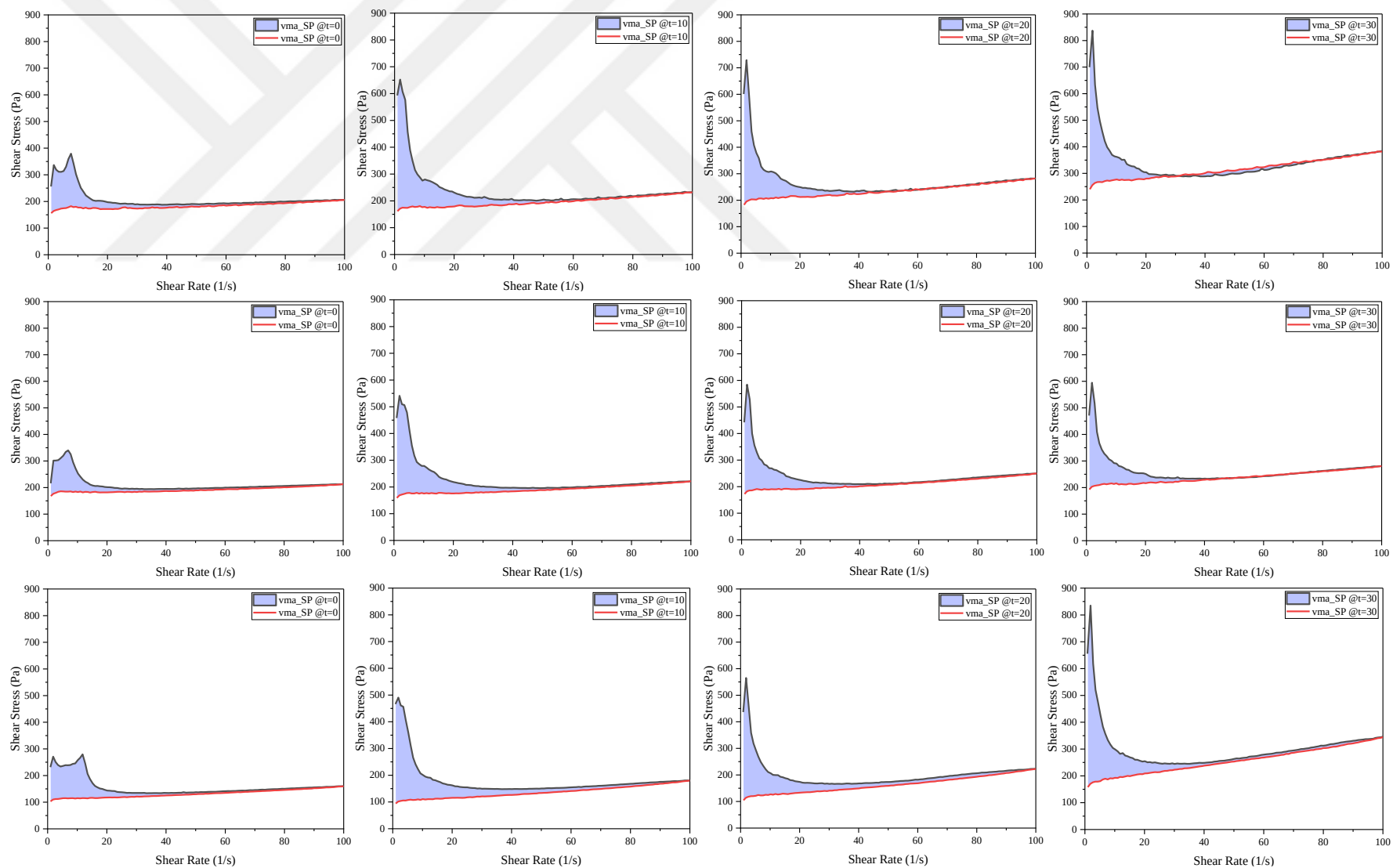


Figure B.5: Hysteresis areas for SEP_1 and SEP_1_FA mixtures obtained at all time intervals. The areas are between the up and down curves, shown in blue color. The plots are in order of increasing time (a) Hysteresis area SEP_1 sample at all time intervals (Trial 1) (b) Hysteresis area for SEP_1 sample at all time intervals (Trial 2) (c) Hysteresis area for SEP_1 sample at all time intervals (Trial 3) (d) Hysteresis area for SEP_1_FA sample at all time intervals (Trial 1) (e) Hysteresis area for SEP_1_FA sample at all time intervals (Trial 2) (f) Hysteresis area for SEP_1_FA sample at all time intervals (Trial 3). SP: Superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (1% of w/w cement weight)



Appendix C – Static Yield

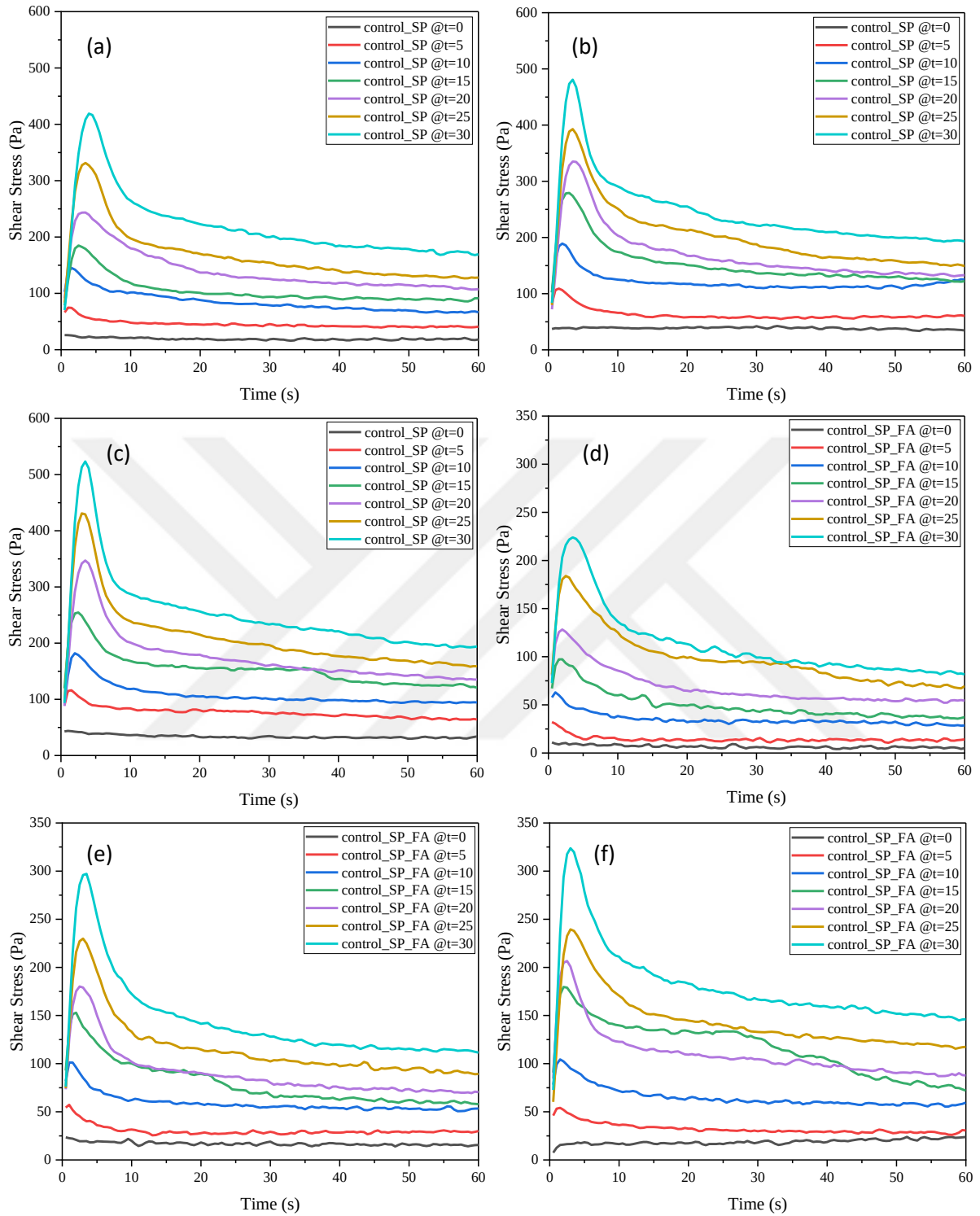


Figure C.1: Shear stress (Pa) vs. time (s) graphs obtained at t=0,5,10,15,20,25,30 (a) shear profile for control_SP sample at different time intervals (Trial 1) (b) shear profile for control_SP sample at different time intervals (Trial 2) (c) shear profile for control_SP sample at different time intervals (Trial 3) (d) shear profile for control_SP_FA sample at different time intervals (Trial 1) (e) shear profile for control_SP_FA sample at different time intervals (Trial 2) (f) shear profile for control_SP_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

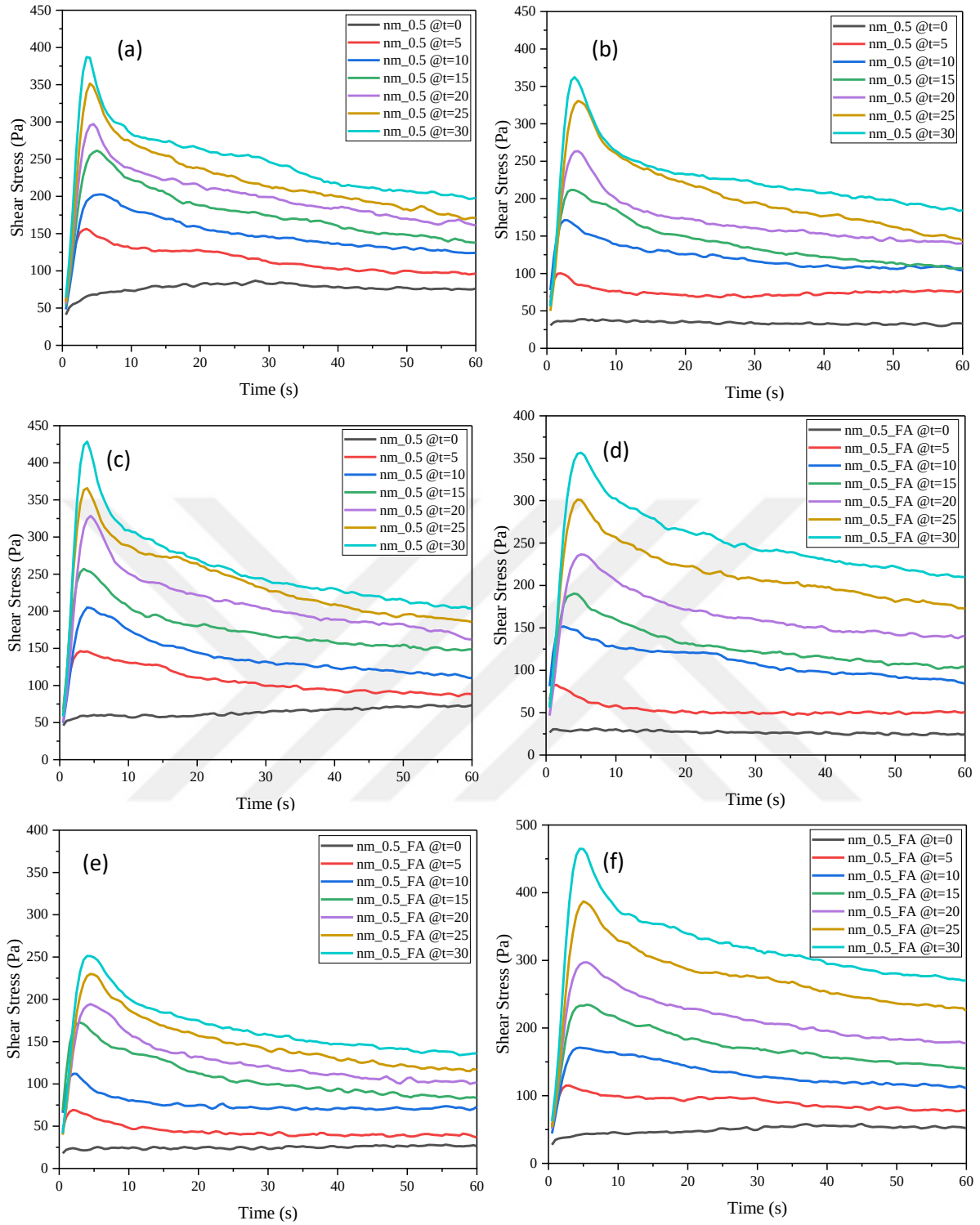


Figure C.2: Shear stress (Pa) vs. time (s) graphs obtained at t=0,5,10,15,20,25,30 (a) shear profile for NM_0.5 sample at different time intervals (Trial 1) (b) shear profile for NM_0.5 sample at different time intervals (Trial 2) (c) shear profile for NM_0.5 sample at different time intervals (Trial 3) (d) shear profile for NM_0.5_FA sample at different time intervals (Trial 1) (e) shear profile for NM_0.5_FA sample at different time intervals (Trial 2) (f) shear profile for NM_0.5_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (0.5% of w/w cement weight)

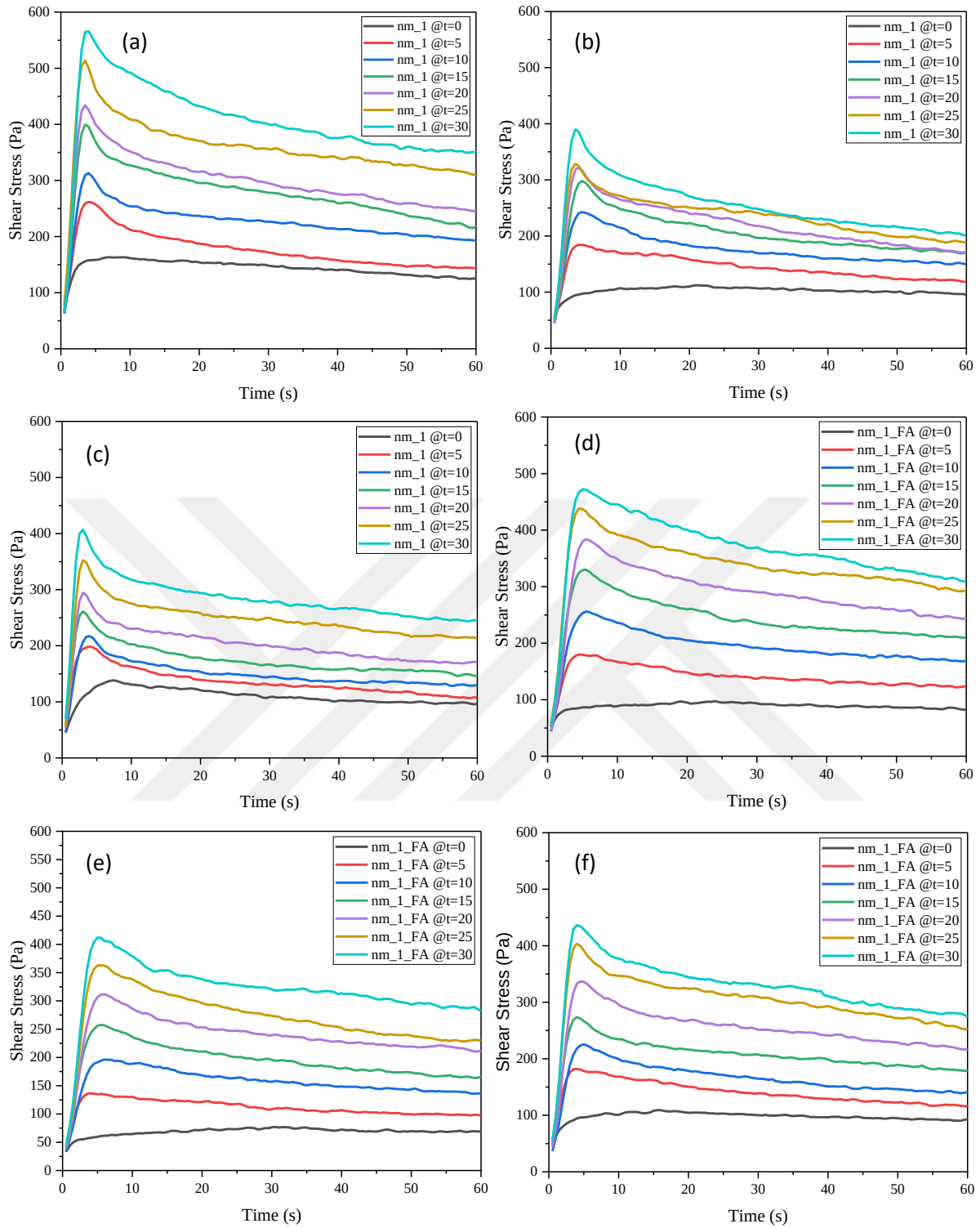


Figure C.3: Shear stress (Pa) vs. time (s) graphs obtained at $t=0,5,10,15,20,25,30$ (a) shear profile for NM_1 sample at different time intervals (Trial 1) (b) shear profile for NM_1 sample at different time intervals (Trial 2) (c) shear profile for NM_1 sample at different time intervals (Trial 3) (d) shear profile for NM_1_FA sample at different time intervals (Trial 1) (e) shear profile for NM_1_FA sample at different time intervals (Trial 2) (f) shear profile for NM_1_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); NM: Nano-montmorillonite (1% of w/w cement weight)

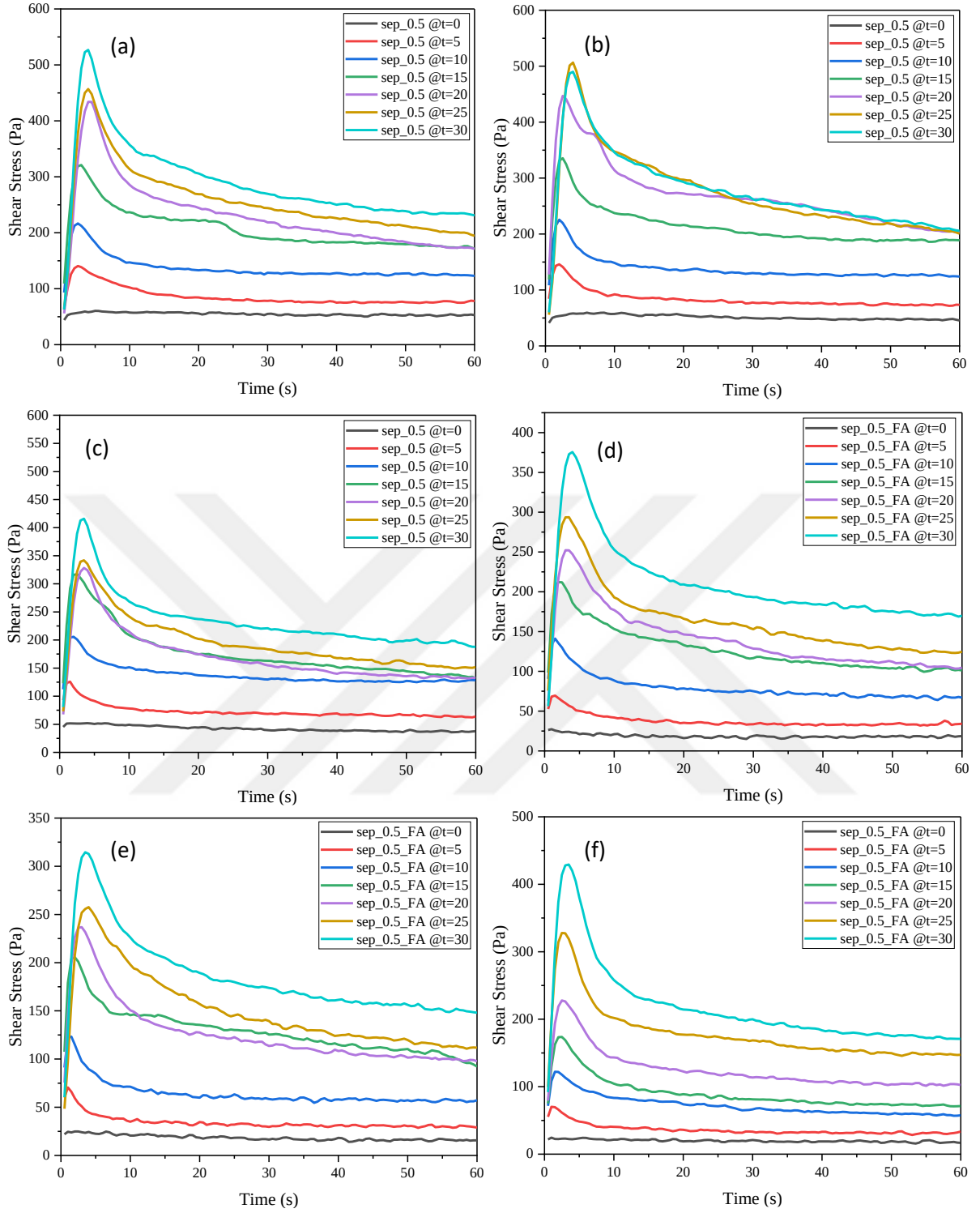


Figure C.4: Shear stress (Pa) vs. time (s) graphs obtained at $t=0,5,10,15,20,25,30$ (a) shear profile for SEP_0.5 sample at different time intervals (Trial 1) (b) shear profile for SEP_0.5 sample at different time intervals (Trial 2) (c) shear profile for SEP_0.5 sample at different time intervals (Trial 3) (d) shear profile for SEP_0.5_FA sample at different time intervals (Trial 1) (e) shear profile for SEP_0.5_FA sample at different time intervals (Trial 2) (f) shear profile for SEP_0.5_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (0.5% of w/w cement weight)

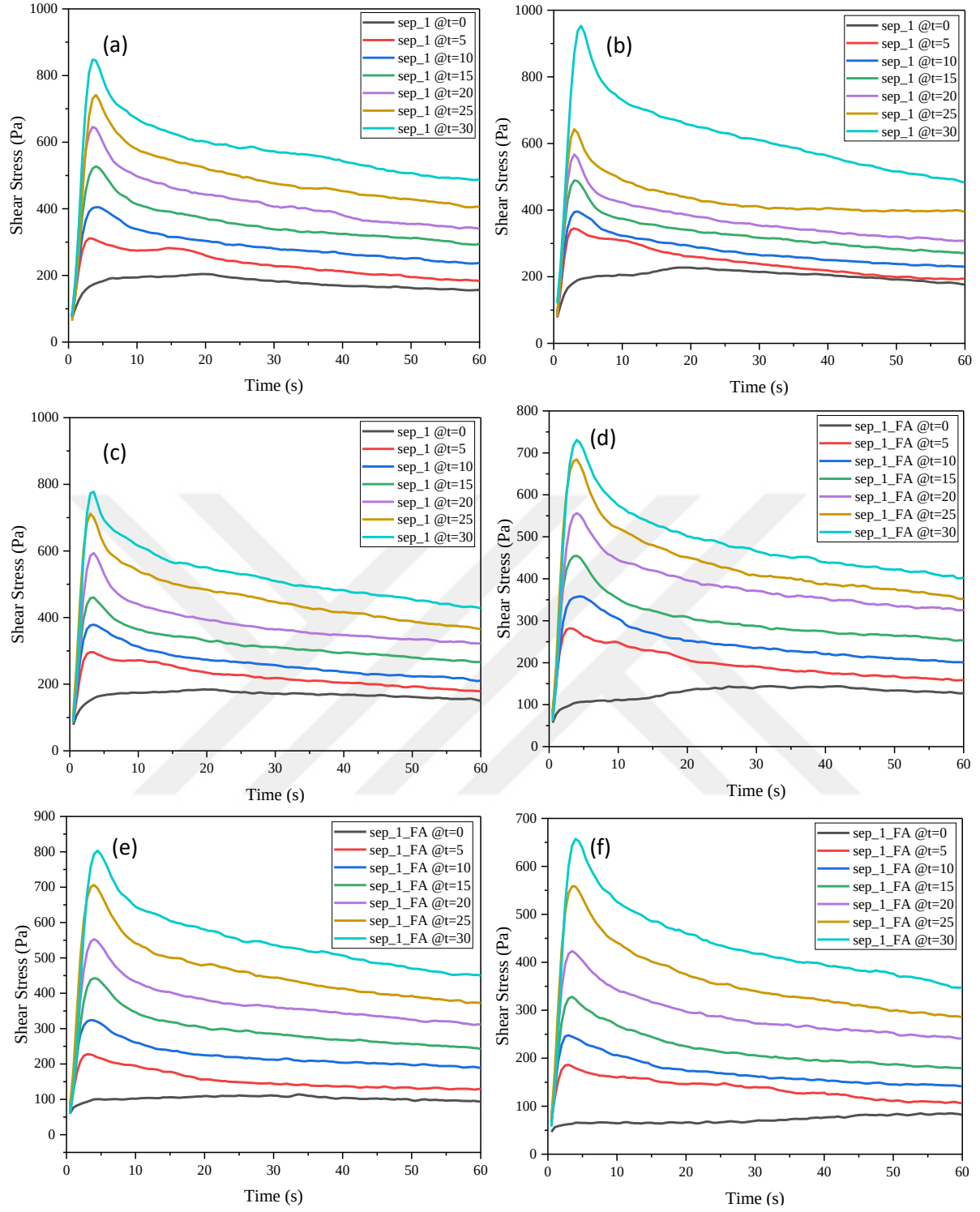


Figure C.5: Shear stress (Pa) vs. time (s) graphs obtained at $t=0,5,10,15,20,25,30$ (a) shear profile for SEP_1 sample at different time intervals (Trial 1) (b) shear profile for SEP_1 sample at different time intervals (Trial 2) (c) shear profile for SEP_1 sample at different time intervals (Trial 3) (d) shear profile for SEP_1_FA sample at different time intervals (Trial 1) (e) shear profile for SEP_1_FA sample at different time intervals (Trial 2) (f) shear profile for SEP_1_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight); SEP: Sepiolite (1% of w/w cement weight)

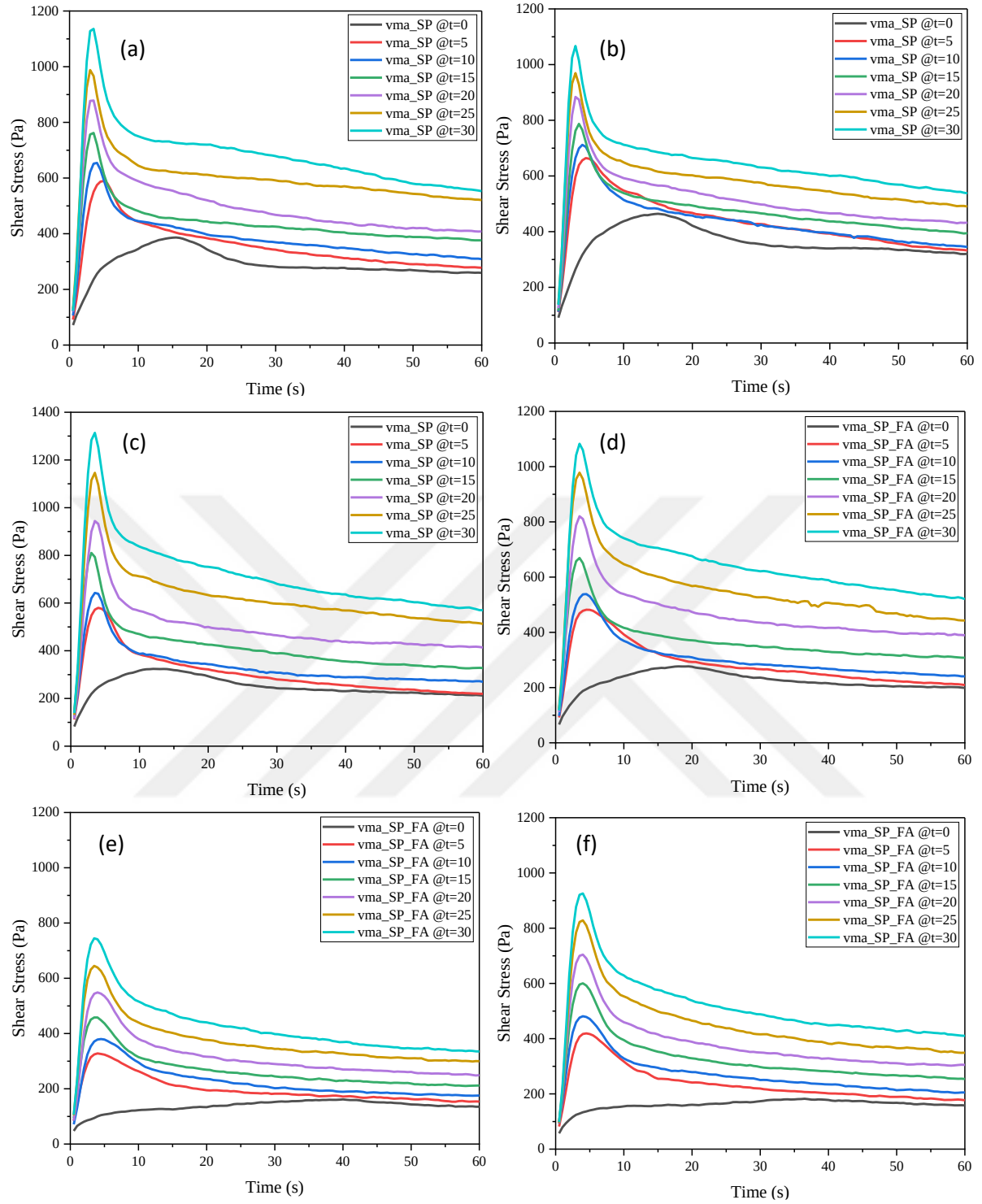


Figure C.6: Shear stress (Pa) vs. time (s) graphs obtained at $t=0,5,10,15,20,25,30$ (a) shear profile for VMA_SP sample at different time intervals (Trial 1) (b) shear profile for VMA_SP sample at different time intervals (Trial 2) (c) shear profile for VMA_SP sample at different time intervals (Trial 3) (d) shear profile for VMA_SP_FA sample at different time intervals (Trial 1) (e) shear profile for VMA_SP_FA sample at different time intervals (Trial 2) (f) shear profile for VMA_SP_FA sample at different time intervals (Trial 3). All mixes contain superplasticizer (0.50% of w/w cement); FA: Fly Ash (20% of w/w cement weight); VMA: Viscosity Modifying Admixture (0.5% of w/w cement weight)

Appendix D -- Apparent Viscosity plots of all mixes

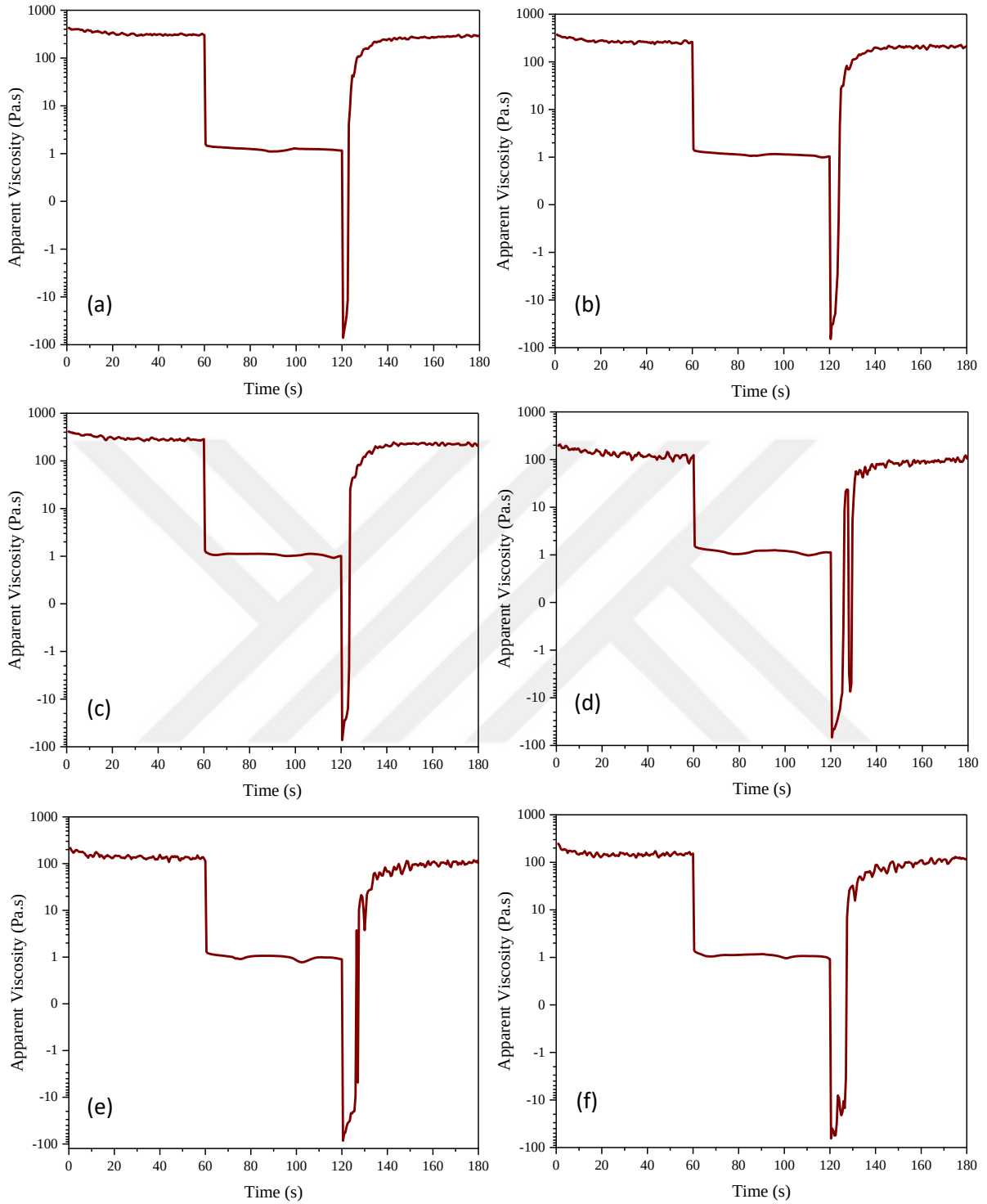


Figure D.1: Effect of different shear rates on apparent viscosity of control samples. a) Apparent viscosity for control_SP sample (Trial 1) (b) Apparent viscosity for control_SP sample (Trial 2) (c) Apparent viscosity for control_SP sample (Trial 3) (d) Apparent viscosity for control_SP_FA sample (Trial 1) (e) Apparent viscosity for control_SP_FA sample (Trial 2) (f) Apparent viscosity for control_SP_FA sample (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight)

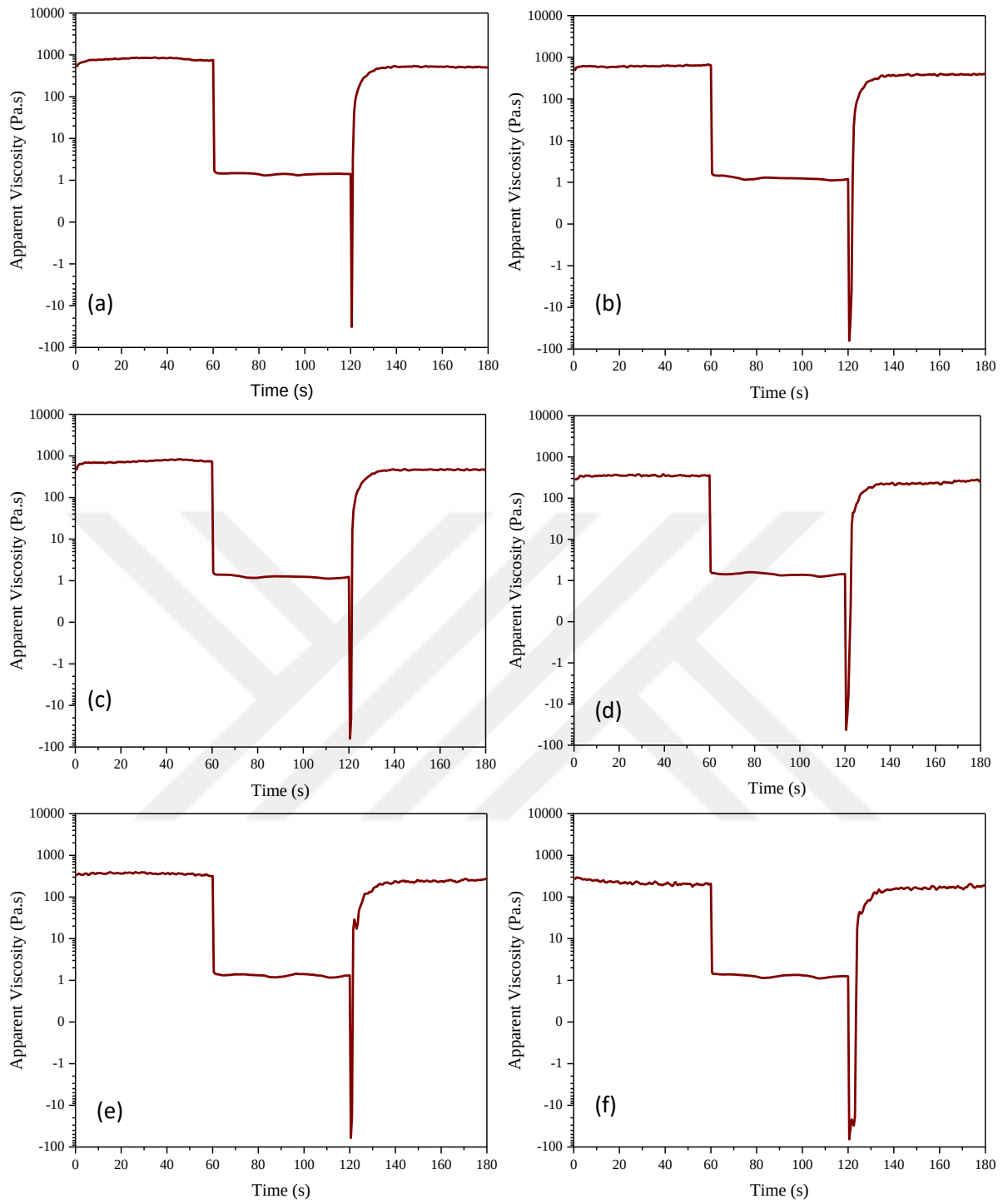


Figure D.2: Effect of different shear rates on apparent viscosity NM containing samples. a) Apparent viscosity for NM_0.5 sample (Trial 1) (b) Apparent viscosity for NM_0.5 sample (Trial 2) (c) Apparent viscosity for NM_0.5 sample (Trial 3) (d) Apparent viscosity for NM_0.5_FA sample (Trial 1) (e) Apparent viscosity for NM_0.5_FA sample (Trial 2) (f) Apparent viscosity for NM_0.5_FA sample (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight; NM: Nano-montmorillonite (0.5% by w/w of cement)

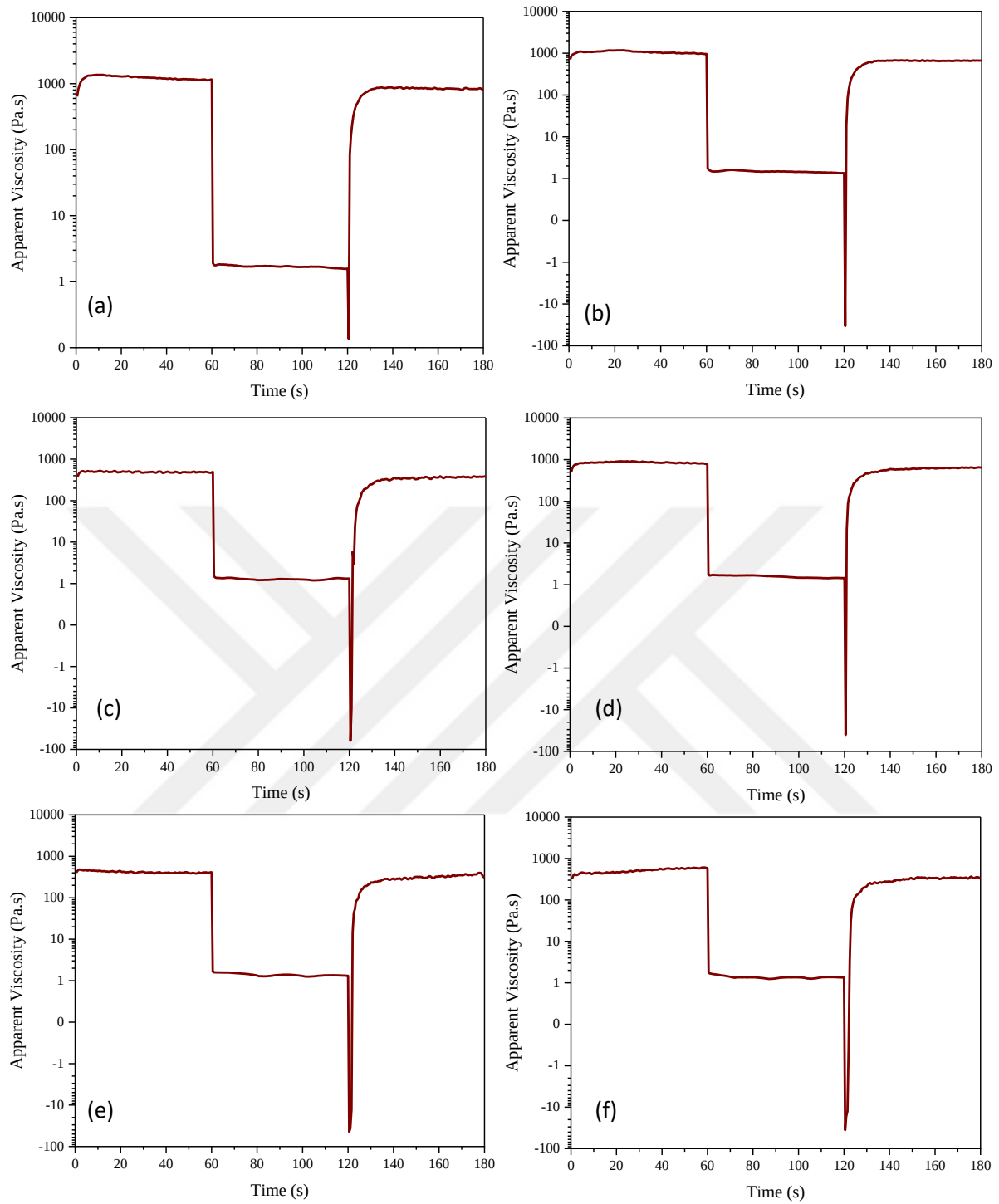


Figure D.3: Effect of different shear rates on apparent viscosity NM containing samples. a) Apparent viscosity for NM_1 sample (Trial 1) (b) Apparent viscosity for NM_1 sample (Trial 2) (c) Apparent viscosity for NM_1 sample (Trial 3) (d) Apparent viscosity for NM_1_FA sample (Trial 1) (e) Apparent viscosity for NM_1_FA sample (Trial 2) (f) Apparent viscosity for NM_1_FA sample (Trial 3). SP: Superplasticizer (0.35% of w/w cement); FA: Fly Ash (20% of w/w cement weight; NM: Nano-montmorillonite (0.5% by w/w of cement)

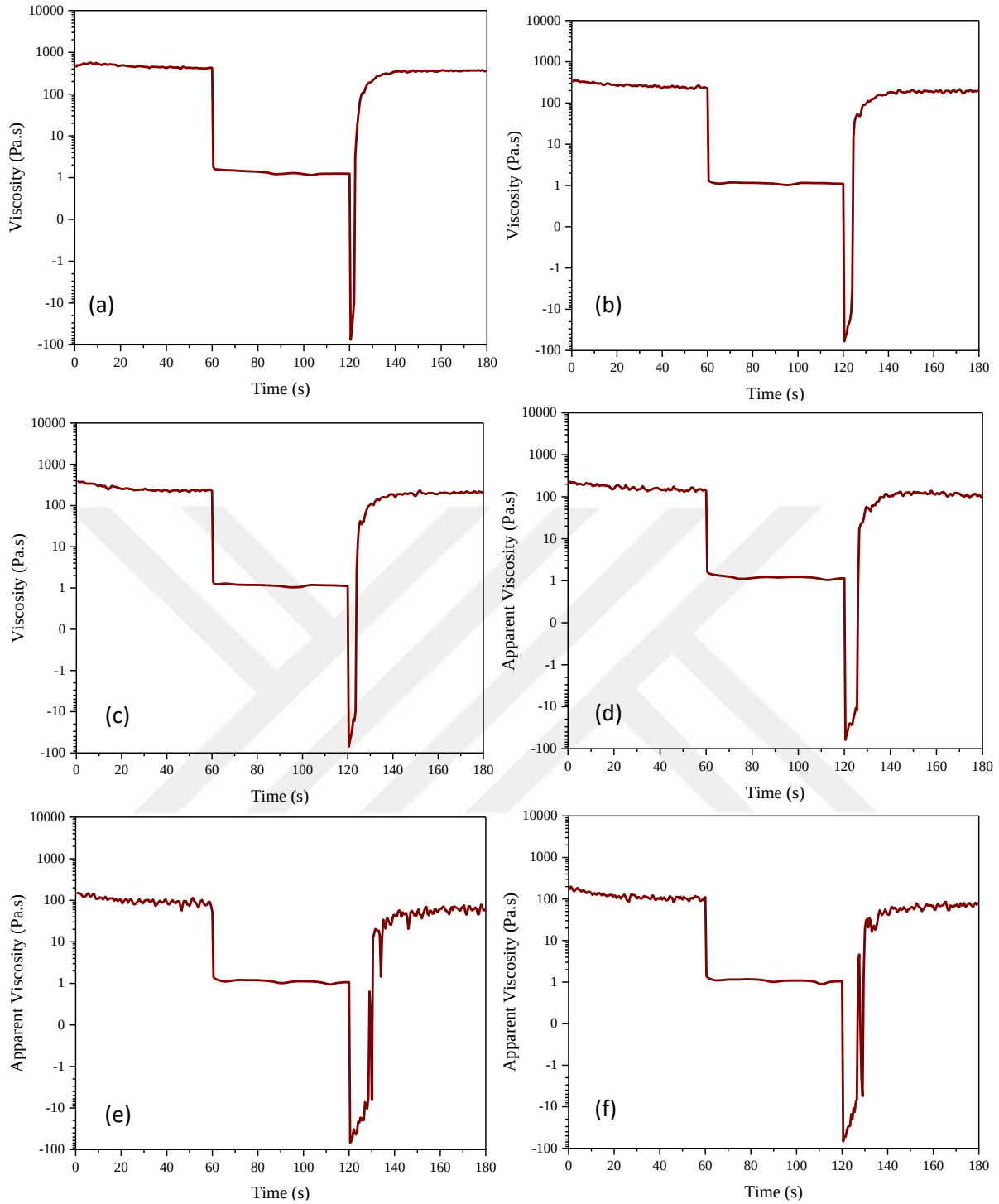


Figure D.4: Effect of different shear rates on apparent viscosity SEP containing samples. a) Apparent viscosity for SEP_0.5 sample (Trial 1) (b) Apparent viscosity for SEP_0.5 sample (Trial 2) (c) Apparent viscosity for SEP_0.5 sample (Trial 3) (d) Apparent viscosity for SEP_0.5_FA sample (Trial 1) (e) Apparent viscosity for SEP_0.5_FA sample (Trial 2) (f) Apparent viscosity for SEP_0.5_FA sample (Trial 3). SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight; SEP: Sepiolite (0.5% by w/w of cement)

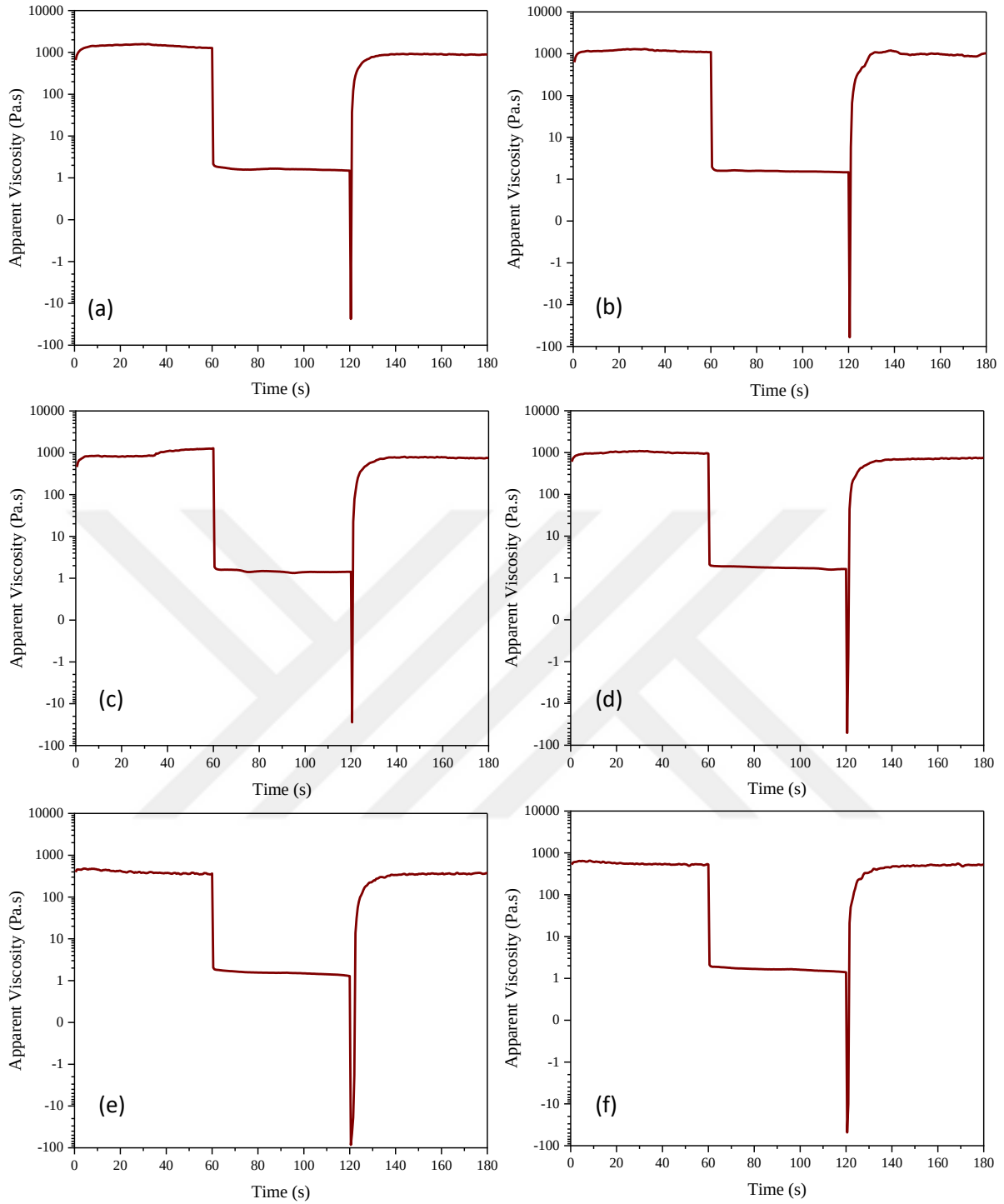


Figure D.5: Effect of different shear rates on apparent viscosity SEP containing samples. a) Apparent viscosity for SEP_1 sample (Trial 1) (b) Apparent viscosity for SEP_1 sample (Trial 2) (c) Apparent viscosity for SEP_1 sample (Trial 3) (d) Apparent viscosity for SEP_1_FA sample (Trial 1) (e) Apparent viscosity for SEP_1_FA sample (Trial 2) (f) Apparent viscosity for SEP_1_FA sample (Trial 3). SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight; SEP: Sepiolite (0.5% by w/w of cement)

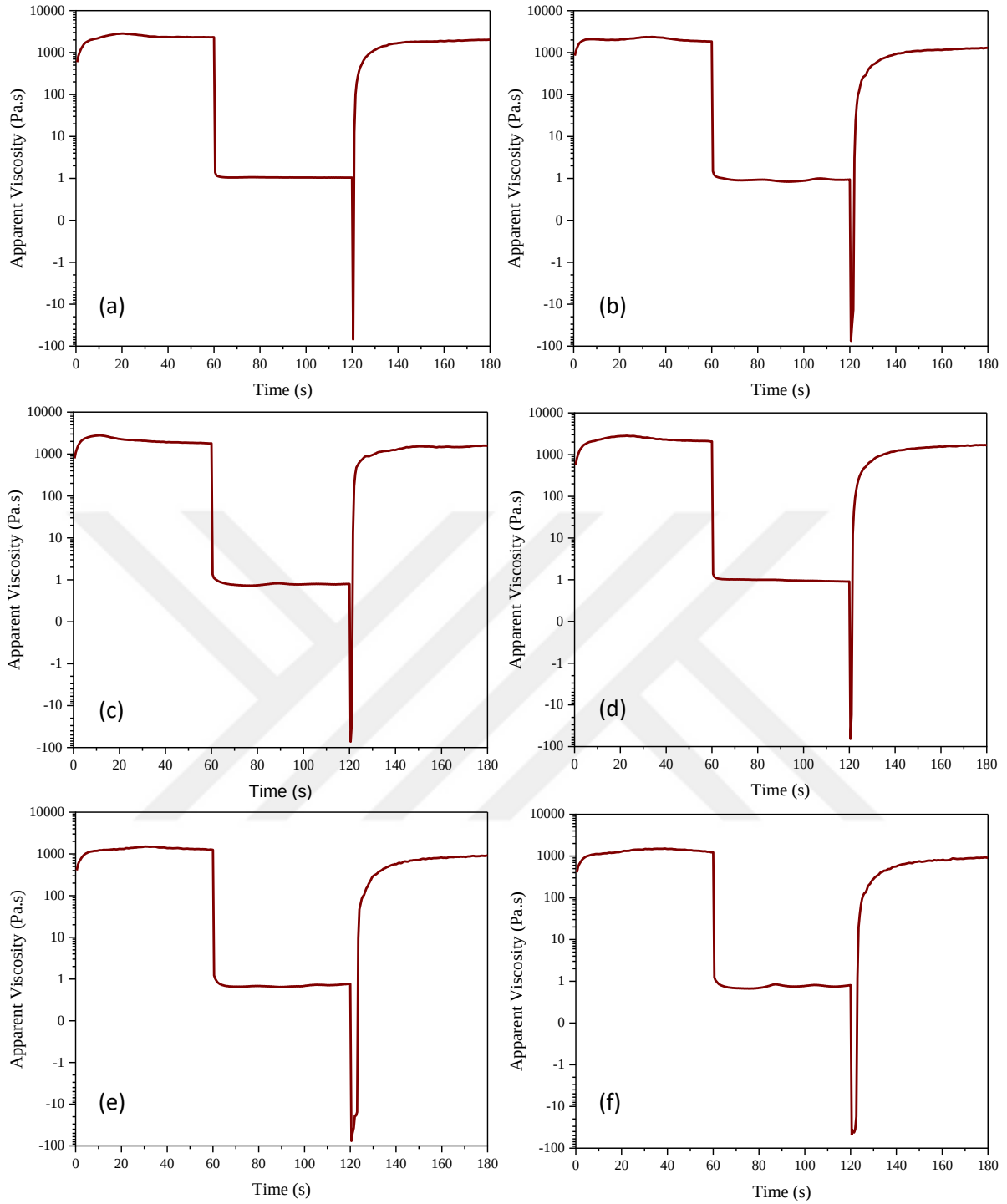


Figure D.6: Effect of different shear rates on apparent viscosity of VMA containing samples. a) Apparent viscosity for control_SP sample (Trial 1) (b) Apparent viscosity for VMA_SP sample (Trial 2) (c) Apparent viscosity for VMA_SP sample (Trial 3) (d) Apparent viscosity for VMA_SP_FA sample (Trial 1) (e) Apparent viscosity for VMA_SP_FA sample (Trial 2) (f) Apparent viscosity for VMA_SP_FA sample (Trial 3). SP: Superplasticizer (0.5% of w/w cement); FA: Fly Ash (20% of w/w cement weight; VMA: Starch ether VMA (0.5% and 1% by w/w of cement)

BIBLIOGRAPHY

- [1] R. A. Buswell, W. R. Leal de Silva, S. Z. Jones, and J. Dirrenberger, “3D printing using concrete extrusion: A roadmap for research,” *Cem. Concr. Res.*, vol. 112, no. October 2017, pp. 37–49, 2018.
- [2] Q. Yuan *et al.*, “A feasible method for measuring the buildability of fresh 3D printing mortar,” *Constr. Build. Mater.*, vol. 227, p. 116600, 2019.
- [3] S. Amziane, Y. Deshpande, R. Ferron, and J. Hu, “ACI 238.2T-14 TechNote Concrete Thixotropy,” no. May 2015, 2014.
- [4] D. Marchon, S. Kawashima, H. Bessaies-Bey, S. Mantellato, and S. Ng, “Hydration and rheology control of concrete for digital fabrication: Potential admixtures and cement chemistry,” *Cem. Concr. Res.*, vol. 112, no. December 2017, pp. 96–110, 2018.
- [5] S. Ng and J. Plank, “Interaction mechanisms between Na montmorillonite clay and MPEG-based polycarboxylate superplasticizers,” *Cem. Concr. Res.*, vol. 42, no. 6, pp. 847–854, 2012.
- [6] M. L. Gambhir, *Concrete Technology*, 5th ed. New Delhi: McGraw Hill Education (India) Private Limited, 2013.
- [7] “Global 3D Concrete Printing Market Information Report, by Concrete Type (Ready Mix Concrete, Precast Concrete, Shotcrete and High Density Concrete), by Application (Residential, Industrial, Agricultural and others), by End-Use (Walls, Roofs, Floor, Stairc,” 2017.
- [8] C. Gosselin, R. Duballet, P. Roux, N. Gaudillière, J. Dirrenberger, and P. Morel, “Large-scale 3D printing of ultra-high performance concrete - a new processing route for architects and builders,” *Mater. Des.*, vol. 100, pp. 102–109, 2016.
- [9] G. De Schutter, K. Lesage, V. Mechtcherine, V. N. Nerella, G. Habert, and I. Agusti-Juan, “Vision of 3D printing with concrete — Technical, economic and environmental potentials,” *Cem. Concr. Res.*, vol. 112, no. June, pp. 25–36, 2018.
- [10] Y. Liu, S. van Nederveen, and M. Hertogh, “Understanding effects of BIM on collaborative design and construction: An empirical study in China,” *Int. J. Proj. Manag.*, vol. 35, 2016.
- [11] B. de Soto *et al.*, “Productivity of digital fabrication in construction: Cost and time analysis of a robotically built wall,” *Autom. Constr.*, vol. 92, 2018.
- [12] J. Otto, J. Kortmann, and M. Krause, “Wirtschaftliche Perspektiven von Beton-3D-Druckverfahren,” *Beton- und Stahlbetonbau*, vol. 115, 2020.
- [13] B. Panda, J. H. Lim, and M. J. Tan, “Mechanical properties and deformation behaviour of early age concrete in the context of digital construction,” *Compos. Part B Eng.*, vol. 165, no. December 2018, pp. 563–571, 2019.
- [14] Z. Li *et al.*, “Fresh and hardened properties of extrusion-based 3D-printed cementitious materials: A review,” *Sustain.*, vol. 12, no. 14, pp. 1–33, 2020.
- [15] S. C. Paul, Y. W. D. Tay, B. Panda, and M. J. Tan, “Fresh and hardened properties of 3D printable cementitious materials for building and construction,” *Arch. Civ. Mech.*

- Eng.*, vol. 18, no. 1, pp. 311–319, 2018.
- [16] A. Kazemian, X. Yuan, E. Cochran, and B. Khoshnevis, “Cementitious materials for construction-scale 3D printing: Laboratory testing of fresh printing mixture,” *Constr. Build. Mater.*, vol. 145, pp. 639–647, 2017.
 - [17] T. Wangler, N. Roussel, F. P. Bos, T. A. M. Salet, and R. J. Flatt, “Digital Concrete: A Review,” *Cem. Concr. Res.*, vol. 123, no. March, 2019.
 - [18] Y. W. D. Tay, G. H. A. Ting, Y. Qian, B. Panda, L. He, and M. J. Tan, “Time gap effect on bond strength of 3D-printed concrete,” *Virtual Phys. Prototyp.*, vol. 14, no. 1, pp. 104–113, 2019.
 - [19] T. Marchment, J. G. Sanjayan, B. Nematollahi, and M. Xia, *Interlayer Strength of 3D Printed Concrete*, no. 3. Elsevier Inc., 2019.
 - [20] T. T. Le, S. A. Austin, S. Lim, R. A. Buswell, A. G. F. Gibb, and T. Thorpe, “Mix design and fresh properties for high-performance printing concrete,” *Mater. Struct. Constr.*, vol. 45, no. 8, pp. 1221–1232, 2012.
 - [21] Y. Qian and G. De Schutter, “Different Effects of NSF and PCE Superplasticizer on Adsorption, Dynamic Yield Stress and Thixotropy of Cement Pastes,” *Materials (Basel)*, vol. 11, p. 695, 2018.
 - [22] B. Panda and M. J. Tan, “3D printing of fiber reinforced cementitious composite modified by PCE and nanoclay,” 2019.
 - [23] B. Łązniewska-Piekarczyk, “Effect of viscosity type modifying admixture on porosity, compressive strength and water penetration of high performance self-compacting concrete,” *Constr. Build. Mater.*, vol. 48, pp. 1035–1044, 2013.
 - [24] K. Khayat, “Viscosity-Enhancing Admixtures for Cement-Based Materials— An Overview,” *Cem. Concr. Compos. - Cem. Concr. Compos.*, vol. 20, pp. 171–188, 1998.
 - [25] M. Palacios and R. Flatt, “Working mechanism of viscosity-modifying admixtures,” 2016, pp. 415–432.
 - [26] Z. Bundur and M. Azima, “A BIO-BASED RHEOLOGY MODIFYING AGENT INSPIRED FROM NATURE,” *Eskişehir Tech. Univ. J. Sci. Technol. A - Appl. Sci. Eng.*, pp. 252–260, 2019.
 - [27] J. H. Jo, B. W. Jo, W. Cho, and J. H. Kim, “Development of a 3D Printer for Concrete Structures: Laboratory Testing of Cementitious Materials,” *Int. J. Concr. Struct. Mater.*, vol. 14, no. 1, 2020.
 - [28] D. Asprone, F. Auricchio, C. Menna, and V. Mercuri, “3D printing of reinforced concrete elements: Technology and design approach,” *Constr. Build. Mater.*, vol. 165, pp. 218–231, 2018.
 - [29] Y. Ju, “Visualization of the three-dimensional structure and stress field of aggregated concrete materials through 3D printing and frozen-stress techniques,” *Constr. Build. Mater.*, vol. 143, pp. 121–137, 2017.
 - [30] Z. Malaeb, F. Alsakka, and F. Hamzeh, “3D concrete printing: Machine design, mix proportioning, and mix comparison between different machine setups,” 2019, pp. 113–136.

- [31] B. Panda, Y. W. D. Tay, S. C. Paul, and M. J. Tan, "Current challenges and future potential of 3D concrete printing," *Materwiss. Werksttech.*, vol. 49, no. 5, pp. 666–673, 2018.
- [32] A. Albar, M. Swash, and S. Ghaffar, "The Design and Development of an Extrusion System for 3D Printing Cementitious Materials," 2019, pp. 1–5.
- [33] M. Hojati *et al.*, "3D Printing of Concrete: a Continuous Exploration of Mix Design and Printing Process," 2018.
- [34] B. Khoshnevis, "Automated construction by contour crafting - Related robotics and information technologies," *Autom. Constr.*, vol. 13, pp. 5–19, 2004.
- [35] B. Khoshnevis, D. Hwang, K.-T. Yao, and Z. Yeh, "Mega-scale fabrication by Contour Crafting," *Int. J. Ind. Syst. Eng.*, vol. 1, 2006.
- [36] A. Jr and F. Santos, "Automatization of the Constructive Process: a Systematic Study of the 3D Concrete Printing Technology (Contour Crafting)," 2019.
- [37] C. Rouhana, M. Aoun, F. Faek, M. El Jazzer, and F. Hamzeh, "The Reduction of Construction Duration by Implementing Contour Crafting (3D Printing)," 2014.
- [38] H. Al Jassmi, F. Al Najjar, and A. H. I. Mourad, "Large-Scale 3D Printing: The Way Forward," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 324, no. 1, 2018.
- [39] "D-Shape: Technology." [Online]. Available: <https://d-shape.com/our-technology/>. [Accessed: 30-Dec-2021].
- [40] "Apis-Cor: Impossible Printing." [Online]. Available: <https://www.apis-cor.com/impossible-printing>. [Accessed: 30-Dec-2020].
- [41] S. Lim *et al.*, "Development of a Viable Concrete Printing Process," 2011.
- [42] G. Ma, Z. Li, and L. Wang, "Printable properties of cementitious material containing copper tailings for extrusion based 3D printing," *Constr. Build. Mater.*, vol. 162, pp. 613–627, 2018.
- [43] V. N. Nerella, M. Krause, and V. Mechtcherine, "Direct printing test for buildability of 3D-printable concrete considering economic viability," *Autom. Constr.*, vol. 109, no. August 2018, p. 102986, 2020.
- [44] R. J. M. Wolfs, F. P. Bos, and T. A. M. Salet, "Early age mechanical behaviour of 3D printed concrete: Numerical modelling and experimental testing," *Cem. Concr. Res.*, vol. 106, no. February, pp. 103–116, 2018.
- [45] Y. Zhang, Y. Zhang, G. Liu, Y. Yang, M. Wu, and B. Pang, "Fresh properties of a novel 3D printing concrete ink," *Constr. Build. Mater.*, vol. 174, pp. 263–271, 2018.
- [46] Y. W. D. Tay, Y. Qian, and M. J. Tan, "Printability region for 3D concrete printing using slump and slump flow test," *Compos. Part B Eng.*, vol. 174, no. May, p. 106968, 2019.
- [47] G. Gibbons, R. Williams, P. Purnell, and E. Farahi, "3D Printing of cement composites," *Adv. Appl. Ceram.*, vol. 109, pp. 287–290, 2010.
- [48] L. Casagrande, L. Esposito, C. Menna, D. Asprone, and F. Auricchio, "Effect of testing procedures on buildability properties of 3D-printable concrete," *Constr. Build. Mater.*,

vol. 245, p. 118286, 2020.

- [49] T. T. Le *et al.*, “Hardened properties of high-performance printing concrete,” *Cem. Concr. Res.*, vol. 42, no. 3, pp. 558–566, 2012.
- [50] B. Zareiyan and B. Khoshnevis, “Effects of interlocking on interlayer adhesion and strength of structures in 3D printing of concrete,” *Autom. Constr.*, vol. 83, pp. 212–221, 2017.
- [51] R. J. M. Wolfs, F. P. Bos, and T. A. M. Salet, “Hardened properties of 3D printed concrete: The influence of process parameters on interlayer adhesion,” *Cem. Concr. Res.*, vol. 119, no. January, pp. 132–140, 2019.
- [52] T. Marchment and J. Sanjayan, “Method of Enhancing Interlayer Bond Strength in 3D Concrete Printing,” in *RILEM Bookseries*, 2019, pp. 148–156.
- [53] B. Zareiyan and B. Khoshnevis, “Interlayer adhesion and strength of structures in Contour Crafting - Effects of aggregate size, extrusion rate, and layer thickness,” *Autom. Constr.*, vol. 81, pp. 112–121, 2017.
- [54] R. J. Flatt and N. Martys, “The Rheology of Cementitious Materials,” pp. 314–318, 2004.
- [55] P. J. Cullen, C. P. O’Donnell, and M. Houška, “Rotational rheometry using complex geometries - A review,” *J. Texture Stud.*, vol. 34, no. 1, pp. 1–20, 2003.
- [56] A. W. Saak, H. M. Jennings, and S. P. Shah, “The influence of wall slip on yield stress and viscoelastic measurements of cement paste,” *Cem. Concr. Res.*, vol. 31, no. 2, pp. 205–212, 2001.
- [57] M. Nehdi and M. A. Rahman, “Effect of geometry and surface friction of test accessory on oscillatory rheological properties of cement pastes,” *ACI Mater. J.*, vol. 101, no. 5, pp. 416–424, 2004.
- [58] D. Han and R. D. Ferron, “Effect of mixing method on microstructure and rheology of cement paste,” *Constr. Build. Mater.*, vol. 93, pp. 278–288, 2015.
- [59] W. G. Lei and L. J. Struble, “Microstructure and flow behavior of fresh cement paste,” *J. Am. Ceram. Soc.*, vol. 80, no. 8, pp. 2021–2028, 1997.
- [60] N. Roussel and H. Bessaies-Bey, “Steady state flows of fresh cement pastes and concretes: Simplified underlying physics,” *Adv. Appl. Ceram.*, vol. 114, no. 7, pp. 402–405, 2015.
- [61] M. Nehdi and M. A. Rahman, “Estimating rheological properties of cement pastes using various rheological models for different test geometry, gap and surface friction,” *Cem. Concr. Res.*, vol. 34, no. 11, pp. 1993–2007, 2004.
- [62] F. J. Rubio-Hernández, “Rheological behavior of fresh cement pastes,” *Fluids*, vol. 3, no. 4, 2018.
- [63] C. Jayasree and R. Gettu, “Experimental study of the flow behaviour of superplasticized cement paste,” *Mater. Struct. Constr.*, vol. 41, no. 9, pp. 1581–1593, 2008.
- [64] M. Bala, R. Zentar, and P. Boustingorry, “Comparative study of the yield stress determination of cement pastes by different methods,” *Mater. Struct. Constr.*, vol. 52,

no. 5, pp. 1–12, 2019.

- [65] A. Yahia and K. H. Khayat, “Analytical models for estimating yield stress of high-performance pseudoplastic grout,” *Cem. Concr. Res.*, vol. 31, no. 5, pp. 731–738, 2001.
- [66] H. A. Barnes, J. F. Hutton, and K. Walters, *An Introduction to Rheology*, 3rd ed. Elsevier Science, 1989.
- [67] N. Roussel, “Rheology of fresh concrete: From measurements to predictions of casting processes,” *Mater. Struct. Constr.*, vol. 40, no. 10, pp. 1001–1012, 2007.
- [68] J. Assaad, K. H. Khayat, and H. Mesbah, “Assessment of thixotropy of flowable and self-consolidating concrete,” *ACI Mater. J.*, vol. 100, no. 2, pp. 99–107, 2003.
- [69] R. P. Ferron, A. Gregori, Z. Sun, and S. P. Shah, “Rheological Method to Evaluate Structural Buildup in Self-Consolidating Concrete Cement Pastes,” no. May, 2007.
- [70] K. Khayat and A. Omran, “Field monitoring of SCC formwork pressure and validation of prediction models,” *Concr Int*, vol. 33, no. May, pp. 33–39, 2016.
- [71] N. Roussel, “A thixotropy model for fresh fluid concretes: Theory, validation and applications,” *Cem. Concr. Res.*, vol. 36, no. 10, pp. 1797–1806, 2006.
- [72] E. Lloret-Fritschi *et al.*, “From Smart Dynamic Casting to a growing family of Digital Casting Systems,” *Cem. Concr. Res.*, vol. 134, no. April, 2020.
- [73] N. Roussel, “Rheological requirements for printable concretes,” *Cem. Concr. Res.*, vol. 112, no. January, pp. 76–85, 2018.
- [74] S. Chaves Figueiredo *et al.*, “An approach to develop printable strain hardening cementitious composites,” *Mater. Des.*, vol. 169, 2019.
- [75] B. Panda, C. Unluer, and M. J. Tan, “Extrusion and rheology characterization of geopolymer nanocomposites used in 3D printing,” *Compos. Part B Eng.*, vol. 176, no. August, p. 107290, 2019.
- [76] B. Panda, N. A. N. Mohamed, S. C. Paul, G. V. P. B. Singh, M. J. Tan, and B. Šavija, “The effect of material fresh properties and process parameters on buildability and interlayer adhesion of 3D printed concrete,” *Materials (Basel)*, vol. 12, no. 13, 2019.
- [77] B. Panda, S. Ruan, C. Unluer, and M. J. Tan, “Improving the 3D printability of high volume fly ash mixtures via the use of nano attapulgite clay,” *Compos. Part B Eng.*, vol. 165, no. November 2018, pp. 75–83, 2019.
- [78] A. V. Rahul, M. Santhanam, H. Meena, and Z. Ghani, “3D printable concrete: Mixture design and test methods,” *Cem. Concr. Compos.*, vol. 97, no. December 2018, pp. 13–23, 2019.
- [79] J. Kruger, S. Zeranka, and G. van Zijl, “An ab initio approach for thixotropy characterisation of (nanoparticle-infused) 3D printable concrete,” *Constr. Build. Mater.*, vol. 224, pp. 372–386, 2019.
- [80] D. G. Soltan and V. C. Li, “A self-reinforced cementitious composite for building-scale 3D printing,” *Cem. Concr. Compos.*, vol. 90, pp. 1–13, 2018.
- [81] B. Panda and M. J. Tan, “Improving 3D printability of fiber reinforced concrete via combined use of PCE-type superplasticizer and nanoclay,” no. November, 2019.

- [82] Y. Chen, Ç. Yalçınkaya, O. Çopuroğlu, and E. Schlangen, “The Effect Of Viscosity Modifier Agent On The Early Age Strength Of The Limestone And Calcined Clay-Based Sustainable And 3D Printable Cementitious Material,” *Proc. 10th Int. Concr. Congr.*, pp. 242–250, 2019.
- [83] Y. Chen *et al.*, “Improving printability of limestone-calcined clay-based cementitious materials by using viscosity-modifying admixture,” *Cem. Concr. Res.*, vol. 132, no. November 2019, 2020.
- [84] Y. Qian, S. Ma, S. Kawashima, and G. De Schutter, “Rheological characterization of the viscoelastic solid-like properties of fresh cement pastes with nanoclay addition,” *Theor. Appl. Fract. Mech.*, vol. 103, no. April, p. 102262, 2019.
- [85] R. Jayathilakage, P. Rajeev, and J. Sanjayan, “Yield stress criteria to assess the buildability of 3D concrete printing,” *Constr. Build. Mater.*, vol. 240, p. 117989, 2020.
- [86] G. S. Slavcheva and O. V. Artamonova, “Rheological behavior and mix design for 3D printable cement paste,” *Key Eng. Mater.*, vol. 799 KEM, pp. 282–287, 2019.
- [87] C. Zhang, Z. Hou, C. Chen, Y. Zhang, V. Mechtcherine, and Z. Sun, “Design of 3D printable concrete based on the relationship between flowability of cement paste and optimum aggregate content,” *Cem. Concr. Compos.*, vol. 104, no. April, p. 103406, 2019.
- [88] A. V. Rahul, M. Santhanam, H. Meena, and Z. Ghani, “Mechanical characterization of 3D printable concrete,” *Constr. Build. Mater.*, vol. 227, p. 116710, 2019.
- [89] J. Xiao *et al.*, “3D recycled mortar printing: System development, process design, material properties and on-site printing,” *J. Build. Eng.*, vol. 32, no. July, p. 101779, 2020.
- [90] E. Güneyisi, M. Gesoğlu, and E. Booya, “Fresh properties of self-compacting cold bonded fly ash lightweight aggregate concrete with different mineral admixtures,” *Mater. Struct.*, vol. 45, 2012.
- [91] Y. Qian and G. De Schutter, “Enhancing thixotropy of fresh cement pastes with nanoclay in presence of polycarboxylate ether superplasticizer (PCE),” *Cem. Concr. Res.*, vol. 111, 2018.
- [92] P. Hosseini, A. Afshar, B. Vafaei, A. Booshehrian, E. Raisi, and A. Esrafil, “Effects of nano-clay particles on the short-term properties of self-compacting concrete,” *Eur. J. Environ. Civ. Eng.*, 2017.
- [93] P. Liu, M. Du, P. Clode, H. Li, J. Liu, and Y.-K. K. Leong, “Surface Chemistry, Microstructure, and Rheology of Thixotropic 1-D Sepiolite Gels,” *Clays Clay Miner.*, vol. 68, no. 1, pp. 9–22, 2020.
- [94] Sigma Aldrich, “Nanoclay, surface modified,” 2020.
- [95] “Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency,” West Conshohocken, PA, 2014.
- [96] M. Rahman, M. Baluch, and M. Malik, “Thixotropic behavior of self compacting concrete with different mineral admixtures,” *Constr. Build. Mater.*, vol. 50, pp. 710–717, 2014.
- [97] Anton Paar, “Basics of thixotropy.” [Online]. Available: <https://wiki.anton->

paar.com/en/basics-of-thixotropy/. [Accessed: 30-Dec-2020].

- [98] M. J. Webster, W. Xiaozheng, and Z. Aisha, “Rheology and Setting Time of Cement Paste,” vol. 3, no. 6, pp. 208–211, 2015.
- [99] M. Azima and Z. Basaran Bundur, “Influence of *Sporasarcina pasteurii* cells on rheological properties of cement paste,” vol. 225, pp. 1086–1097, 2019.
- [100] A. M. Ley-Hernández, D. Feys, and A. Kumar, “How do different testing procedures affect the rheological properties of cement paste?,” *Cem. Concr. Res.*, vol. 137, no. June, p. 106189, 2020.
- [101] T. Wangler *et al.*, “Digital Concrete: Opportunities and Challenges,” *RILEM Tech. Lett.*, vol. 1, p. 67, 2016.
- [102] K. . Khayat and A. Yahia, “Simple field tests to characterize fluidity and washout resistance of structural cement grout,” *Cem. Concr. Aggregates*, vol. 20, no. 1, pp. 145–156, 1998.
- [103] M. Sonebi, “Rheological properties of grouts with viscosity modifying agents as diutan gum and welan gum incorporating pulverised fly ash,” *Cem. Concr. Res.*, vol. 36, no. 9, pp. 1609–1618, 2006.
- [104] M. Lachemi, K. M. A. Hossain, V. Lambros, P. C. Nkinamubanzi, and N. Bouzoubaâ, “Self-consolidating concrete incorporating new viscosity modifying admixtures,” *Cem. Concr. Res.*, vol. 34, no. 6, pp. 917–926, 2004.
- [105] K. H. Khayat and M. Saric-Coric, “Effect of Welan Gum-Superplasticizer Combinations on Properties of Cement Grouts,” *Spec. Publ.*, 2000.
- [106] H. Karimi, F. Gauvin, H. J. H. Brouwers, R. Cardinaels, and Q. Yu, “On the versatility of paper pulp as a viscosity modifying admixture for cement composites,” *Constr. Build. Mater.*, vol. 265, p. 120660, 2020.
- [107] L. Reiter, T. Wangler, A. Anton, and R. Flatt, “Setting on demand for digital concrete – Principles, measurements, chemistry, validation,” *Cem. Concr. Res.*, vol. 132, 2020.
- [108] J. Pinilla Melo, A. Sepulcre Aguilar, and F. Hernández Olivares, “Rheological properties of aerated cement pastes with fly ash, metakaolin and sepiolite additions,” *Constr. Build. Mater.*, 2014.
- [109] C. Wu and S. Kou, “Effects of high-calcium sepiolite on the rheological behaviour and mechanical strength of cement pastes and mortars,” *Constr. Build. Mater.*, vol. 196, pp. 105–114, 2019.
- [110] K. Katti and D. Katti, “Effect Of Clay-Water Interactions On Swelling In Montmorillonite Clay,” *Civ. Eng.*, vol. 9, no. August, pp. 1–9, 1997.

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