STUDIES ON POLYMER NANOCOMPOSITES AS SHEAR THICKENING FLUIDS

A

Thesis

Submitted for fulfillment of the Degree

of

Doctor of Philosophy

By

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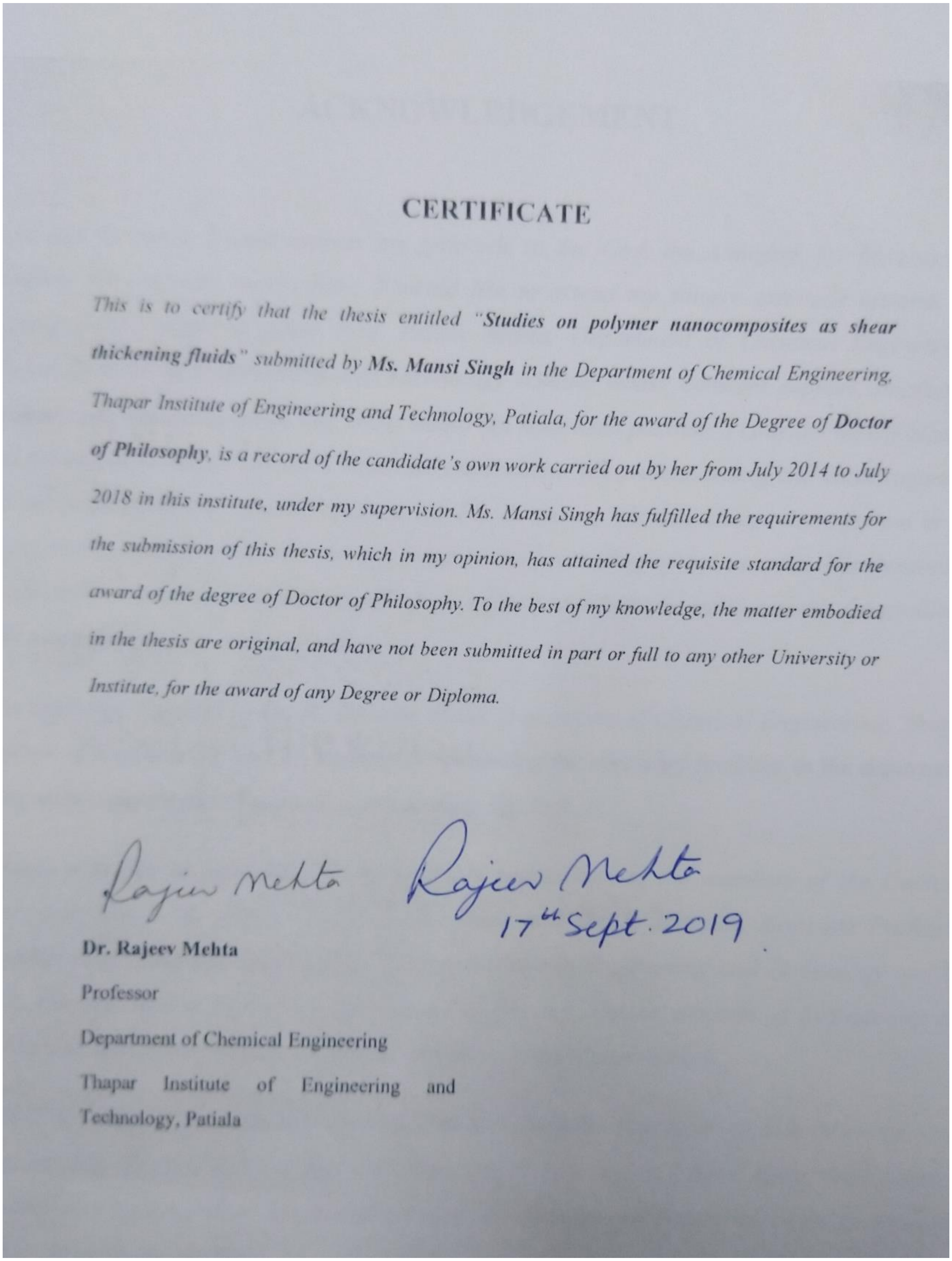
This thesis is dedicated to my parents, my dearest brother and my friends, for giving their constant and unyielding support and for being my source of strength.



CERTIFICATE

*This is to certify that the thesis entitled "**Studies on polymer nanocomposites as shear thickening fluids**" submitted by **Ms. Mansi Singh** in the Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala, for the award of the Degree of **Doctor of Philosophy**, is a record of the candidate's own work carried out by her from July 2014 to July 2018 in this institute, under my supervision. Ms. Mansi Singh has fulfilled the requirements for the submission of this thesis, which in my opinion, has attained the requisite standard for the award of the degree of Doctor of Philosophy. To the best of my knowledge, the matter embodied in the thesis are original, and have not been submitted in part or full to any other University or Institute, for the award of any Degree or Diploma.*

Rajeev Mehta Rajeev Mehta
17th Sept. 2019

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ABSTRACT

The shear thickening fluids (STF) are dispersions of hard inorganic particles in a liquid medium with a unique combination of properties and are well known for their ability to absorb large impact shear/forces along with reduced weight. When STF is subjected to an impact, at typically high shear rates, it suddenly exhibits a discontinuous increase in viscosity with reversibility. Thus, STF can be utilized in the design of control and damping devices including shock absorbers for sports equipment, clutches, brakes and seismic protectors for buildings etc, due to its ability to self-limit maximum rate of flow. There has been a lot of interest in using STF in liquid body armor by impregnating high performance aramid fabrics such as Kevlar with STF. The impregnated body armor could provide rigidity for resisting piercing by stabbing knife blows, bullets and similar attacks yet allowing the flexibility and reduced weight to the wearer. For shear thickening properties at high shear rates, the attractive forces (depletion and hydrodynamic forces) should be higher than repulsive forces (electrostatic and polymer stabilization forces) in the STF suspensions. The STF reported in literature containing hard inorganic particles dispersed in low viscosity polymers prevent the use of STF for all conditions as they do not provide shear thickening at extreme conditions due to small range of operating shear rates. Modification of conventional STF with improved elasticity and stability is very important and can be used to develop STF for improved or new applications.

There are several approaches that can be used to modify the properties of STF. Two typical approaches for this can be distinguished. The first approach involves modifying the hydrodynamic forces by adding high aspect ratio particles and the second approach involves modifying the particle-liquid interaction and depletion forces by refining the liquid medium properties with liquids having specific chemical functionality such as high viscosity polymers. Aforesaid STF would combine the material properties of the additives. Current trends towards nanoparticles and viscoelastic polymers make performance of STF increasingly relevant. Thus, improvement of existing STF by additives provides an elegant route towards STF having new and advanced properties.

In the present study the primary raw materials and processing conditions for STF have been extensively studied. Fumed silica (11nm) in Polyethylene glycol (PEG) having molecular weight 200g/mol, gives high shear thickening properties at very low concentrations as compared to dispersion of simple silica particles (400nm). Furthermore, considerable improvement in stability is seen for fumed silica samples with respect to sedimentation and shear thickening properties over time as compared to simple silica. The probe sonication of 10 minutes for 20ml sample of 20% fumed silica PEG-STF is an effective method to attain uniform and homogeneous dispersion and prior sonication for 2 min is required for dispersing clay particles in PEG. The 20% STF of fumed silica PEG demonstrated a better and stable dispersion as well as shear thickening properties suitable for studying the effect of different particles and liquids as additives.

The rheological behaviors of STF have been investigated as these new STF exhibited better shear thickening behavior with respect to different parameters. Significantlly, the additives provide an opportunity to vary the shear thickening range of STF. The findings suggest that these STF could be useful for varying engineering applications where a range of critical viscosity and critical shear rate are required.

Building on the base STF material of 20% of fumed silica in PEG200, the present study reports desirable viscoelastic behavior for the STF with different additives. The concentrations of these additives are much lower than fumed silica concentration. Among the nanoclays, MMT, Kaolin, Halloysite, NanomerI.28E and Closite®15A along with alumina particles were used as additives, Closite®15A and NanomerI.28E demonstrated significant enhancement in shear thickening properties in the steady as well as dynamic state and appreciable stability at low and high temperatures. Among different high molecular weight PEGs i.e. PEG4600, PEG6000 and PEG10000, as additives to PEG200, PEG with molecular weight of 6000 showed promising properties.

Silicone oil of different viscosity, namely, 100, 500 and 1000cst in different concentrations were added to the primary liquid medium (PEG200) for processing of STF. Silicone oil being hydrophobic in nature required modification with PEG to interact with hydrophilic fumed silica therefore, silicone oil has only been used as additive. As viscosity of silicone oil increases, STF properties (critical viscosity) increase but at the cost of dispersion of fumed silica particles and stability with respect to temperature due to an increase in gel like behavior. Additionally, suspension of hydrophobic fumed silica as primary particles instead of hydrophilic fumed silica with PEG200 and PPG425 (polypropylene glycol; molecular weight 425g/mol) have been studied. Hydrophilic fumed silica dispersed in semi-polar PPG causes an intense increase in value of critical viscosity at very low shear rates that confirm slight gel like behavior and later transforms to a gel after a week of storage whereas hydrophobic fumed silica in PPG gives smooth shear thickening properties with high stability.

In general, it was found from steady-state rheology results that with an increase in temperature and time of storage, the shear tickening behavior decreases i.e critical values of viscosity decreases a lot. This decrease in shear thickening is more pronounced in high molecular weight PEGs and high viscosity silicone oil added as additives as compared to nano-clays and alumina particles added as additives.

Shear thickening fluids have been studied under steady-shear deformations as well as oscillatory or dynamic shear deformations under different amplitudes and frequencies. As shear thickening phenomena is dependent on the velocity of impact (time rate of deformation), thus both strain and frequency sweep studies are also very important. Dynamic shear results showed that as concentration of additives increase, dynamic state parameters i.e. storage and loss modulus also increase and this increase is very significant for high molecular weight polymers used as additives compared to clay used as additives. It can be concluded that the distinct particles and liquids for STF may leads to diverse effects and sensitivity towards temperature as well as stability.

Thus, cost effective and material utilization improvements can be made by using combination of fumed silica/silica and clays as dispersed particles and high molecular weight and high viscosity liquids as dispersion medium. Also significantly, the different compositions of STF show a vast range of critical viscosity and shear rates, and present work will serve as a valuable resource to select the tunable compositon as per the requirements for different existing and new applications.

ABBREVIATIONS USED

STF	Shear thickening fluids
ST	Shear thickening
AR	as-received
CNT	Carbon nanotube
MMT	Montmorillonite
OMMT	Organo-modified montmorillonite
FTIR	Fourier transform infrared spectrometer
Pa.s	Pascal-second
SEM	Scanning electron microscopy
SA	Surface area
TEM	Transmission electron microscopy

LIST OF SYMBOLS

Nomenclature	**Description**
δ	Phase angle
η_c	Critical viscosity
γ_c	Critical shear rate
$\dot{\gamma}_c$	Critical shear strain
η^*	Complex viscosity
G''	Shear loss modulus
G'	Shear storage modulus
G^*	Complex shear modulus
γ	Strain
Φ_{eff}	Effective volume fraction
Φ_s	Specific volume fraction
σ	Shear stress

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Chapter 1 Introduction

STF constitute a particular class of smart fluids, which combine two desirable properties, namely viscous and elastic. STF owe their popularity to the abundance of popular applications: damping devices, body armor and many more. Silica dispersed in polyethylene glycol has been a common STF. In the recent research use of many raw materials had started picking up. Due to poor reproducibility and consistency in the properties of a typical STF, the range of applications is limited. The methods to increase the shear thickening properties are required due to the need for STF in many novel applications. Shear thickening fluids became a widely researched topic since last two decades and there have been various developments in the experimental study of STF and improvement in its ability in energy absorption. Many researchers have focused on application development work in the field of viscous dampers, shock absorbers, and body armors. A lot of research is still dedicated to improving properties of these materials. Control of shear thickening behavior and stability of the STF are very important in the manufacturing of energy absorbing products. Alternatives for enhancing the shear thickening properties of STF have been studied in the present study by addition of different additives (particles and liquids) in typical STF.

1.1 Shear Thickening Fluids (STF)

The shear thickening material is a smart material in which after a critical value of strain and stress the viscosity increases with the rate of shear strain and stress. Aforesaid *shear thickening fluid, STF,* often observed in concentrated colloidal dispersions is a non-Newtonian fluid as the value of viscosity increases with the applied shear stress. It is a kind of colloidal dispersion whose rheological property changes abruptly when encountering a high impact [1]. At low shear stresses or shear rate STF generally exhibit a shear thinning behavior. When the shear stress is increased after a critical value, the viscosity of STF increases undergoing a transformation from shear thinning to shear thickening behavior [2]. This increment can be gradual or drastic. However, the increment of viscosity is reversible that is when the shear stress is eliminated from the material, immediately its viscosity will start to decrease [2]. In shear thickening fluids electrostatic forces due to simple coulomb interaction between the particles along with polymer stabilization forces due to polymer adsorption on the surface of particles become dominant at no shear conditions (Figure 1.1). At high shear, the attractive forces become dominant where due to the movement of colloidal particles hydrodynamic forces increases additionally the presence of non-adsorbing polymer molecules in the suspension increases the depletion forces. This behavior is controlled by a number of factors such as particle size, shape, and distribution. A number of studies [3-5] on rheological behavior of STF under steady and dynamic shear conditions have been conducted.

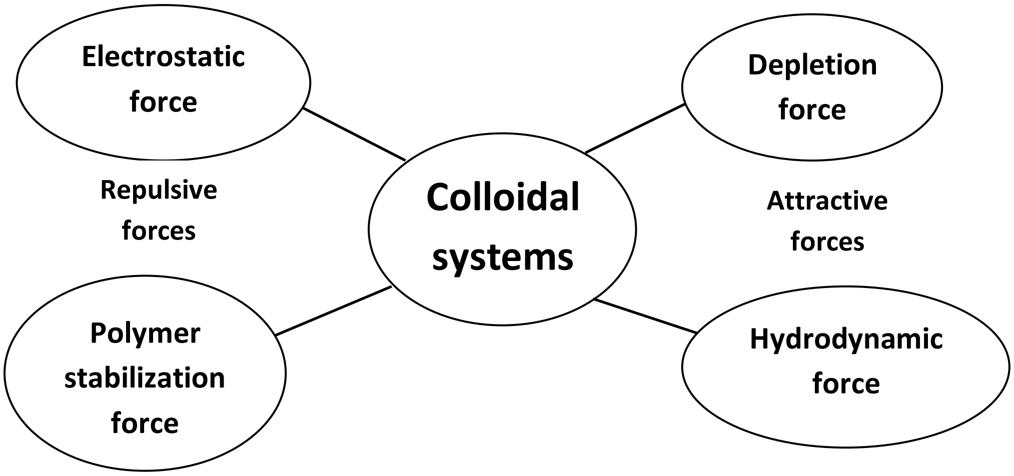

Figure 1.1 Forces acting in a colloidal system

1.2 Benefits and limitations of STF

STF show some impact resisting properties due to their distinctive rheological properties which make them exceptional for certain specified applications. They are used as shock absorbers in damping and protective types of equipment for shielding purposes such as soft armor body, sports padding equipment [2]. One of the most important applications of STF that may take place in future is in the field of liquid body armor production. Since the use of liquids in place of conventional different layered armors will make them cost-effective, lightweight, flexible and easy to wear making them much more beneficial. It was known that process parameter like temperature, dispersion time and dispersion method, effect the rheological properties of STF and also their potential application as shear thickening fabric composite.

The downside of these STF are their inherent sensitivity to various environmental factors such as exposure to liquids/gases, temperature, and the time of storage. Static and dynamic mechanical stresses can interact with environmental frameworks and accelerate the degradation activity. It is widely known that polymeric composites and polymers absorb liquids when exposed to surrounding liquid environments, and the fluid absorption is accompanied by expansion strains which may cause degradation of material properties. Additionally, the absorption of moisture may degrade the fiber-STF interface in liquid body armor. New applications in damping devices and body armor and more stringent demands drive towards the need of specialty STF, with a relatively high impact resisting properties with a relatively low concentration of raw materials.

1.3 Applications of STF

- **Developing bulletproof soft body armor**

  Up to date, the most important application of the STF is for liquid body armors for military purposes. The materials which are used for body armor applications currently are not capable to provide protection of whole body due to their and bulkiness and stiffness. A novel soft body armor based on the STF has shown promising results including improved flexibility and protection. STF improves various properties of fabrics such as tensile strength, load and stress transfer [3]. Most soft body armors in recent researches were formed by impregnating STF (silica-PEG) in a porous media or a fibrous substrate [4, 5].
- **Driving fluids**

  For enhanced oil recovery to plug well-bore blowouts, STF (cornstarch-water) are used as driving fluids due to its property of self-limiting maximum rate of flow [6].
- **Machine mounts**

  Smart flexible devices could be fabricated for which, the stiffness or hardness of a component can change such as from elongation, bending, torque, twisting, or compression as a result of deformation. The STF (silica-ethanol) materials could be used as a means to control mechanical impulse of one object relative to another [7].

- **Damping devices**

  Damping devices filled with a STF include shock absorbers and seismic protectors for buildings (Twaron impregnated silica-PEG STF), clutches, brakes actuators for the automotive industry [8, 9]. Also, a viscoelastic damper was invented to control the vibration of a tank, a pipe, various structural member etc caused by an earthquake or wind [10, 11]. When the speed of the motion is small the STF could present relatively small resistance and could produce progressive resistance as the speed of the motion increases. STF could be immersed into pads for sports equipments for improved energy dissipation, reducing the likelihood of dental damage as mouth guards; gloves for protecting the hands from vibrational or jarring impact; sports shoe designs.

- **Artificial joints and trauma pads**

  Devices could be designed to use STF (cornstarch - water STF) disposed within it for restricting movement of joints such as shoulder, knee, elbow, ankle, hip, etc., so as to prevent the person from subjecting the joint to sudden quick acceleration and subsequent force on the affected area. Aforesaid devices (foam based STF) would help to prevent the damage resulting from rapid acceleration and would work with varying degrees of effectiveness [12].

- **Space suits**

  Research is going on for integration with extra-vehicular activity (EVA) suit and thermal micrometeoroid garment (TMG) replacing conventional neoprene coated nylon covering for protection against micrometeoroids and orbital debris (MMOD) [13].

1.4 Materials used in STF

The common materials that have been used in the production of STF in the literature are evenly dispersed nano-silica particles in PEG [14-16] or PPG [11, 17, 18], silica species, polymethylmethacrylate (PMMA) and calcium carbonate [19], Kaolin clay and cornstarch etc. Fumed silica is a preferred dispersed particle for preparation of STF because of its excellent response against shear forces. Additionally, polypropylene glycol (PPG) [20], polyethylene glycol (PEG) [21], water, glycerol have been used as preferred continuous phase [22].

The structure and properties of all materials used in the present study are as follows:

1.4.1 Dispersed particles

1.4.1.1 Silica

Silicon dioxide, also called silica, is an oxide of silicon with the chemical formula SiO_2 (Figure 1.2). Silica is most commonly found in nature as quartz. It is the major constituent of sand. Silica is also present in a highly complex form in various minerals and can also be produced synthetically. All its parameters such as particle size, surface area, pore size, pore volume etc. vary according to its different forms. It is the major component of STF because of its enormous surface area and its tendency to show thickening and thixotropic properties. They may contain adsorbed H_2O and CO_2 which is removable by calcining at a temperature greater than 900°C.

$$O = Si = O$$

Figure 1.2 The molecular structure of Silica

1.4.1.2 Fumed silica

Hydrophilic fumed silica

Fumed silica particles are produced by the flame hydrolysis process of silicon tetrachloride in an oxyhydrogen gas flame to produce molten spheres of silicon dioxide, therefore it is also known as pyrogenic silica.

$$SiCl_4 + 2H_2 + O_2 \xrightarrow{1500^0 C} SiO_2 + 4HCl$$

With this process, submicron-sized silica spheres collide and of which 40-60% fuse into branched and chain-like primary particles linked to each other through hydrogen bonding and which agglomerate subsequently (0.1-0.2 microns long). Thus primary particles result in the formation of a network structure, due to its chain-like morphology and surface chemistry. Fumed silica is an amorphous and hydrophilic substance which has a high surface area and very low bulk density [23]. Hydrophilicity is provided by the hydroxyl (–OH) groups which cover approximately 40% of its surface. These groups also give the fumed silica its unique shear thickening property. Remaining groups on the surface of the fumed silica are siloxane and silanol groups. They can be dispersed easily in PPG and PEG and characterized by high moisture absorption.

Hydrophobic fumed silica

Hydrophobic fumed silica is prepared by the chemical reaction of hydrophilic fumed silica with reactive silanes e.g. chlorosilanes or hexamethyldisilazane amine oxide (Figure 1.3). It is water repellent i.e. cannot be dispersed in water hence they cannot be dispersed easily in PPG and PEG and characterized by low moisture absorption.

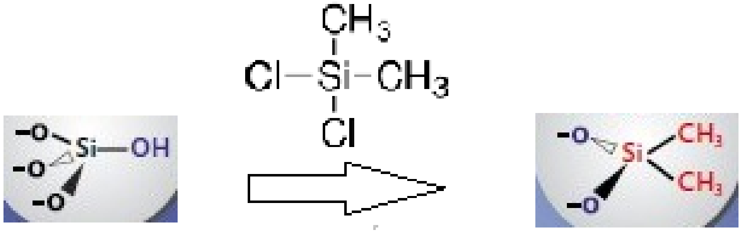

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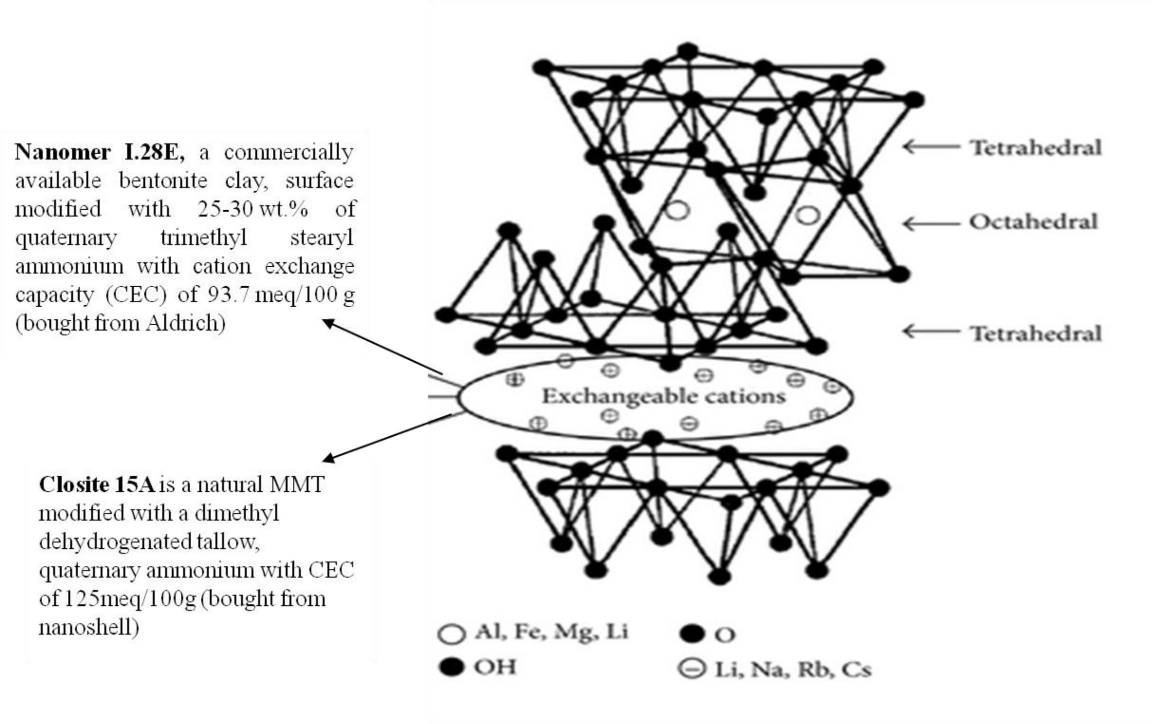
Figure 1.3 Chemical reactions showing the conversion of hydrophilic fumed silica to hydrophobic fumed silica

1.4.1.3 Nanoclay particles

Clay particles are aluminosilicates and they show chemical properties similar to those of silica particles, and are therefore compatible with silica particles [24]. They have unique thermal and mechanical properties, high aspect ratio and therefore, a large surface area of contact with liquid medium is possible in STF. In a low shear rate regime, alignment in the flow direction is easy and large clustering of particles takes place at high shear rates.

MMT clay

MMT clay is naturally occurring 2 : 1 layered smectite clay mineral with a typical chemical structure shown in Figure 1.4 and chemical composition of $A_{0.3}(Al_{1.3}Mg_{0.7})[Si_4]O_{10}(OH)_2H_2O$, where "A" is an exchangeable cation, K^+, Na^+, or $0.5Ca^{2+}$. Montmorillonite consists of ~ 1 nm thick alumino-silicate layers surface-substituted with metal cations and stacked in ~ 10 µm sized multilayer stacks. Depending on the surface modification of the clay layers, montmorillonite can be dispersed in a polymer matrix to form polymer-clay nanocomposite. Within the nanocomposite individual, nm-thick clay layers become fully separated to form plate-like nanoparticles with very high aspect ratio. Nanomer® I.28E and Closite®15A are organically modified MMT clay with a different modifier and CEC (cation exchange capacity) [25, 26].



Nanomer I.28E, a commercially available bentonite clay, surface modified with 25-30 wt.% of quaternary trimethyl stearyl ammonium with cation exchange capacity (CEC) of 93.7 meq/100 g (bought from Aldrich)

Closite 15A is a natural MMT modified with a dimethyl dehydrogenated tallow, quaternary ammonium with CEC of 125meq/100g (bought from nanoshell)

Figure 1.4 Organically modified MMT clay [24]

Kaolin clay

Kaolin clay is chemically $Al_2Si_2O_5\ (OH)_4$, Aluminum Silicate Hydroxide. Kaolin's structure (Figure 1.5) is composed of silicate sheets (Si_2O_5) bonded to aluminum oxide/hydroxide layers ($Al_2(OH)_4$). The difference between MMT clay and Kaolin clay is described in Table 1.1.

Halloysite clay

Halloysite shares the same chemistry as the mineral Kaolin as they are polymorphs as shown in Figure 1.5. Halloysite is natural aluminosilicate clay with hollow tubular morphology and has an average dimension of 15 × 1000 nm comparable to carbon nanotubes as shown in Figure 1.6. Halloysite nanotubes typically have internal diameter of 50 nm and width lengths ranging from 0.5 to 1 microns, giving high aspect ratio.

Table 1.1 Description of Kaolin and MMT clays [26]

	Kaolin	**Montmorillonite (MMT)**
Type of clay	1:1	2:1
Structure of layers	Octahedral alumina sheet sitting on the top of the silica tetrahedral sheet.	One octahedral alumina sheet is sandwiched between two tetrahedral silica sheets.
Interlayer space	Two layers are bonded by strong Oxygen – Hydrogen linkage: OH	Interlayer space consists of sodium and potassium cations.
Swelling nature	Non-swelling as consists of many aggregately strong hydrogen bonds that do not expand or swell.	Swelling due to absorption of extra water in their interlayer.

Some of the advantages of Halloysite clay are: Naturally exfoliated morphology means easier dispersions; non toxic biocompatible; 15-18 w/w % structurally bound water trapped between each layer; low thermal diffusivity; potential barrier to oxygen; large aspect ratio and small size means higher strength and stiffness; non-abrasive and therefore will not damage fiber material when intercalated with protective fiber for body armor applications of STF. Table 1.2 shows the aspect ratio of all three structurally different clays.

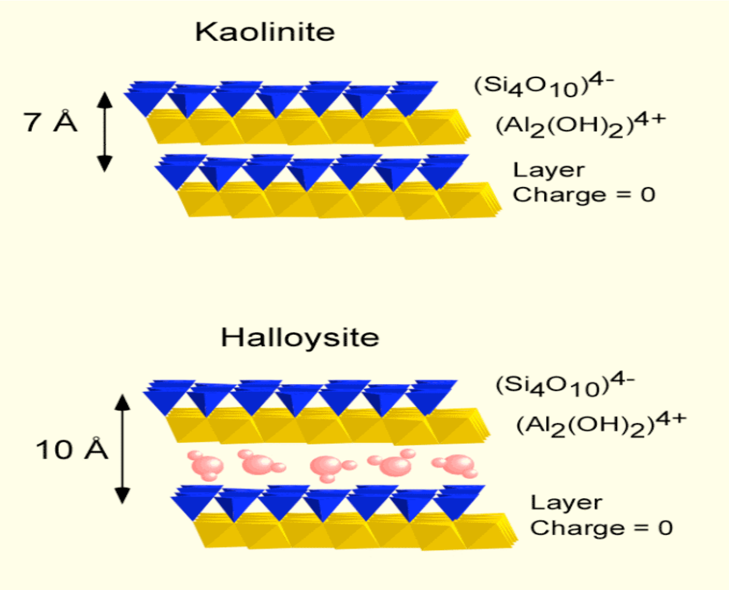


Figure 1.5 Comparison of Kaolinite and Halloysite clay structure [27]

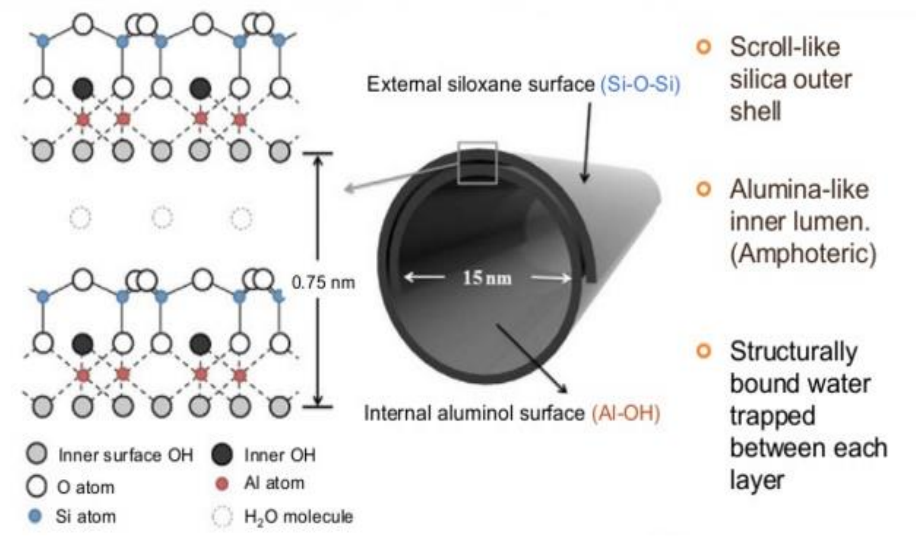


Figure 1.6 Halloysite clay structure [25]

Table 1.2 Aspect ratio of different clays [28]

Nanoclay	MMT	Kaolin	Halloysite
Aspect ratio	10-30	4-6	10-20

1.4.1.4 Alumina particles

In metal oxides, the surface of a solid crystal is a truncated area of the crystal consisting of coordinately unsaturated site anions and cations. For this reason, when a metal oxide is exposed to the atmosphere, the outer layer becomes covered with the abundant component, such as water. This absorbed water can be present at the surface in the form of the terminal OH groups. Among the different metal oxide nanoparticles, Alumina (Al_2O_3) or aluminum oxide, has a range of useful properties, including good thermal conductivity, high strength, and stiffness, mechanical strength, inertness to most acids and alkalis, high adsorption capacity, wear resistance, oxidation, thermal stability and so on. In addition, it is inexpensive, non-toxic, and highly abrasive to the fabric [29-31]. These physiochemical properties propose Al_2O_3 nanoparticles with great potential to be used in STF and to investigate the effect of pure oxides on the rheological properties.

1.4.2 Dispersion medium

1.4.2.1 Polyethylene glycol

Generally, polymers and particularly high molecular weight or viscosity polymers are well known to show both viscous and elastic nature. PEG (Figure 1.7) is a low viscosity water-soluble synthetic polar organic compound which is commercially available in the molecular weight range of 200 to 20,000 g/mole. It is also non-toxic and easy to handle, thermally stable and easily available in bulk quantities which make it useful for bulk production.

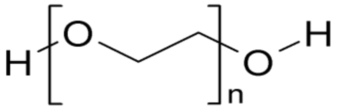


Figure 1.7 Polyethylene Glycol

Polyethylene glycols are available in a range of low to medium molecular weight polyethers having primary hydroxyl groups at each end. PEG is also known as Polyethylene oxide (PEO) or Polyoxyethylene (POE), depending on its molecular weight [32-34]. All polyethylene glycols are completely soluble in water. Some major features of polyethylene glycol are: good solvent action; good stability; good lubricating property; very low toxicity; highly compatible with other compounds. Its uses as organic media in STF production is widely known. According to literature, PEG hydrogen bonds well with the Kevlar fibers making it suitable carrier fluid for making STF for liquid body armor use. Additionally, PEG has refractive index matching with silica thus, with silica results in a stable sol. It was also assumed that high molecular weight PEG at high shear rates will be able to create 3-D network between the silica particles and polymer chains due to branched structure and long molecules resulting in a large increase in viscosity values.

1.4.2.2 Polypropylene glycol

Polypropylene glycol (PPG) or polypropylene oxide is the polymer of propylene glycol (Figure 1.8). PPG has many properties in common with polyethylene glycol. The polymer is a liquid at room temperature. Solubility in water decreases rapidly with increasing molar mass. Secondary hydroxyl groups in PPG are less reactive than primary hydroxyl groups in polyethylene glycol. PPG is less toxic than PEG. PPG is used as a rheology modifier and used as a surfactant, wetting agent, dispersant in leather finishing. The propylene glycol molecule is quite stable and doesn’t decompose over time.

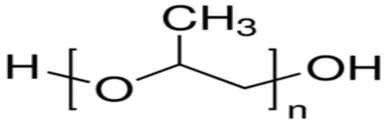


Figure 1.8 Chemical structure of Polypropylene glycol

1.4.2.3 Silicone oil

Silicone is a synthetic hydrophobic polymeric compound made up of silicon, oxygen, and other elements, generally, carbon and hydrogen (Figure 1.9). Silicones have a set of unique properties that divide them from all other kinds of polymers: able to form longer chains without solidifying due to more flexible molecular chains; more resistant to harsh environmental conditions (stable in the temperature range of -50 to 150^{0}C), as well as processing and operating conditions due to stronger and more stable bonds; and low viscosity- temperature coefficient i.e. viscosity changes very little with temperature. It is almost unaffected by the presence of aluminum, stainless steel, and most of the other materials used for body armor and is chemically inert and non-toxic [35]. Beyond this, silicones have high shear resistance, can bridge particles farther apart due to its longer chains and can attach to a greater number of particles and increases the degree of bridging [36].

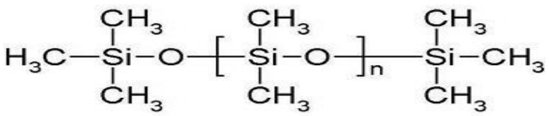


Figure 1.9 Chemical structure of Silicone oil

1.5 Rheology

Rheology is the study of the flow of matter in a liquid state, also as 'soft solids' or under conditions in which solid rather than deforming elastically respond with the plastic flow in response to an applied force. Rheology primarily accounts for the behavior of non-Newtonian fluids, by identifying the minimum number of functions which are required to relate stress response with a rate of change of strain.

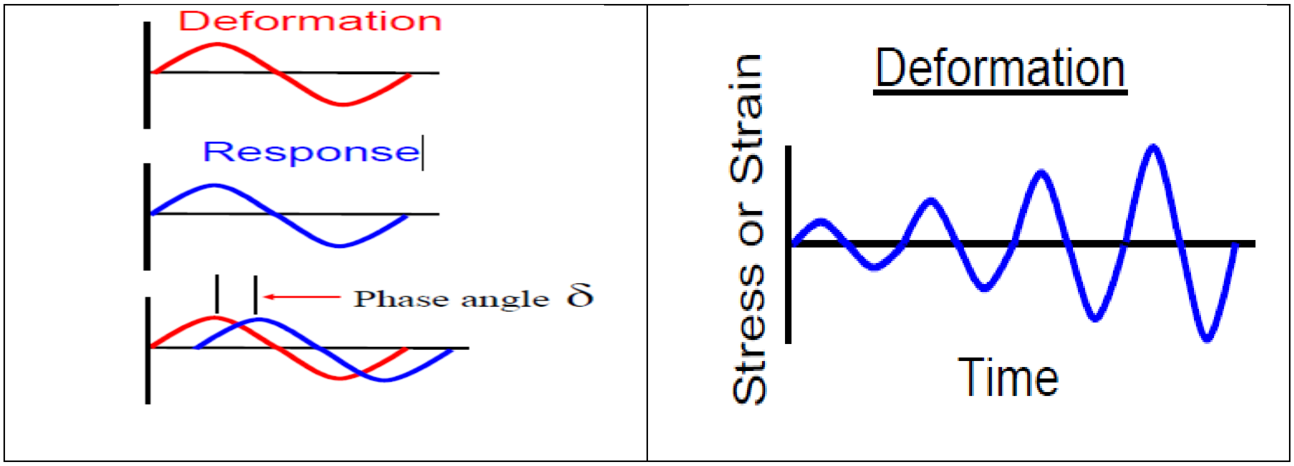
The instrument that is used to measure the responses of materials under applied forces is a rheometer . Rheometers are used with different geometries such as parallel plate and cone and plate of plate diameter and different cone angle. With steady-shear and dynamic shear measurements the effect of shear stress on the behavior of STF can be observed.

1.5.1 Steady-state shear rheology

Steady-state shear rheological measurements are conducted to observe the bulk viscosity and equilibrium microstructure of materials with only minor disturbance. Under steady-state shearing, the microstructure deformation increases with increasing applied shear rate [37]. The rheological profiles of steady-state shear viscosity verses shear rate at different temperatures were studied for STF.

1.5.2 Dynamic-state shear rheology

Dynamic-state shear rheological measurements of materials allow to observe the viscoelastic properties in terms of complex modulus. In dynamic-state measurements, the material is being vibrated between two plates (cone and plate or parallel-plate) and a sinusoidal oscillation of strain or stress is applied to the sample material. Different modes dynamic-state measurements are conducted such as frequency sweep, strain sweep and time sweep. The shear thickening phenomena is being dependent on the velocity of impact (time rate of deformation) as composition become semi-solid or solid during the impact, thus, both strain and frequency sweeps are equivalently important to be studied. In order to investigate the structural properties, the effect of increasing strain/stress on the values of complex viscosity and complex modulus at constant frequencies is studied for investigating material response (stress/strain) to increasing deformation strain at a constant frequency and temperature. Complex modulus can be divided into imaginary and real parts which are viscous modulus (G") and elastic modulus (G') respectively. The viscous (loss) modulus is the ability of the material to dissipate energy (as heat) i.e. $G''=(stress^*/strain)\sin\delta$, and the elastic (storage) modulus is the ability of the material to store energy i.e $G'=(stress^*/strain)\cos\delta$ where δ is the frequency of oscillation and $stress^*$ is dynamic stress. The complex modulus is the measure of materials overall resistance to deformation i.e. $G^* = Stress^*/Strain$; $G^* = G' + i\,G''$. Thus the loss and storage modulus both together characterize the viscoelastic behavior. Tan delta or damping factor is the measure of damping (vibration or sound) of the material i.e. $Tan\,(delta) = G''/G'$ and the complex viscosity is the complex modulus divided by the frequency [38].



(a) (b)

Figure 1.10 Pictorial representation of the measurement of deformation and response in oscillatory rheology (a) showing a phase difference (b) at a varying amplitude with a constant frequency [38].

Shear thickening behavior remains mainly difficult to characterize using rheological measurements carried out generally at low deformation and frequency, as the shear thickening phenomena is a non-linear response mainly triggered by either high frequency or large deformation. As a consequence, in recent research, the characterization of STF has been extended to high strain and frequency values [39]. For both steady-state as well as dynamic state rheology, pre-shear/strain is important for achieving a better dispersion of particles and to remove any previous history of shear during processing and loading sample to rheometer. Then after pre-shearing rest time is given to sample to equilibrate thermally and to restore possible structures [40].

At this stage, the synopsis of the present work is given in the following section.

1.6 Synopsis

The present study sheds light on STF, its raw materials, the optimum concentration of particles, the optimum time for processing and effect of different nano-additives in the typical STF. Further, the effect of different parameters like temperature, shear rate, strain and frequency of deformation has been monitored using a rheometer. The modification of STF has been divided into three consecutive form (1) nanoclays and nano-alumina as particle additives (2) high molecular weight PEGs and high viscosity silicone oil as additives to liquid medium (3) hydrophilicity of particles. The different research topics discussed in the chapters are categorized under one of this modification type. The study embodies the subject matter resulting out of the rheological profiles and is arranged in eleven separate chapters. The outline of the chapters is given below:

Chapter 1: This chapter starts with a general introduction to STF and converges to the need for developing STF with additional properties like light weight and stability using different materials and additives. Further, the effect of temperature is discussed. Lastly, the significance and need for a highly optimized STF are established by highlighting the drawbacks of the existing STFs.

Chapter 2: It provides a literature review incorporating the latest STF studies suggesting that the studies of STF are still sparse. Also, many investigators have not considered the parameters like temperature, particle morphology, particle-surface chemistry etc. that can control shear thickening in these suspensions.

Chapter 3: This chapter lists all the particles and carrier fluids that can be used for processing shear thickening suspensions along with their properties. In addition, details regarding procedure followed to prepare the STF have been discussed using a flowchart.

Chapter 4: Firstly, this is a discussion about the various STF that were processed using different raw materials and processes in order to evaluate the optimum concentration and type of raw materials and the duration of dispersion. Further, it details the method of dispersing clay particles in PEG. The rheological results clearly showed that due to fractal nature of fumed silica, effective volume fraction of disperse phase is observed to be appreciably more, resulting in shear thickening at low volume fraction (20%) as compared to 60% for simple silica. This has significant implication for the STF application where reduced weight would be important.
Addition of clays enhances the shear thickening effect in both silica and fumed silica STF. Fumed silica (11 nm) suspensions are stable for more than 1 month since no sedimentation was visually observed but nano silica (400 nm) suspension do show phase separation after one month. On the other hand, pure STF could not be obtained by dispersing clays in PEG 200 and or

glycerol. Thus, nanoclay can only be used as additives in STF of fumed silica and PEG. Only Kaolin clay shows some shear thickening at very low value of critical shear rate with glycerol which may be due to the fact that Kaolin are non- swelling clays as they consist of many strong hydrogen bonds that do not expand or swell.

Further, it was observed that nano-dispersion and exfoliation of clay particles in PEG before addition of fumed silica particles is very important for enhancing shear thickening properties. In addition, optimum sonication time for sonicator probe for 20% fumed silica suspensions was found to be about 10 min. Besides this, the results demonstrate that 20% by weight fumed silica particles provided an optimum combination of low viscosity at zero–shear, marked shear thickening, relatively high-post-transformation viscosity and also ease of dispersion and relative stability with the consistency of results. For this reason, 20% concentration of silica-PEG STF was selected as a base for all further studies with different additives.

Chapter 5: The modification of STF by additives is typically aimed at enhancing the elasticity, thereby improving the stability of STF and compatibility of both dispersing medium (solvent) and dispersed phase (particles) with each other. Different ways to modify the shear thickening properties of typical STF are thoroughly discussed herein. The first way is to increase the hydrodynamic forces by nanoclay particles as an additive to base STF, which is highlighted in this chapter with their possible interactions with the PEG and the fumed silica particles. It is worthwhile to report that rod-shaped Kaolin clay (Halloysite) as additive shows a large critical viscosity at all temperatures as compared to layered Kaolin clay and the viscosity increases significantly with an increase in concentration. Furthermore, the critical viscosity of modified MMT (Closite®15A) is more than unmodified MMT but the increase in shear thickening properties is less with an increase in concentration, which may be due to difficulty in the proper dispersion of high concentration of modified clay as an additive.

Moreover, Kaolin and Halloysite clay as additives show a large increase in critical viscosity as compared to MMT and Closite®15A respectively due to their non-swelling properties.

Lastly, dynamic study shows that Closite®15A as an additive gives high values of all the parameters (complex viscosity, loss modulus, and storage modulus) which confirms the highly viscoelastic nature of this STF as compared to all other additives. Further, a large increase in storage modulus (elasticity) as frequency increases from 10 to 30 rad/s confirms a high degree of crosslinked (physically) structure resulting in high impact resistance properties.

Chapter 6: In this chapter rheology of another organically modified MMT clay, Nanomer I.28E as nano-additive is studied when mixed with base/reference STF under a wide range of temperature, shear rate, strain rate and frequency. This system was found to exhibit significant improvement over only fumed silica- shear thickening fluids under similar processing conditions. The idea of using clay is of interest from the perspective of resource utilization, increased performance and environmental concerns. Specifically, it was inferred that the addition of nanoclay to base STF leads to a decrease in critical viscosity compared to the same concentration of fumed silica when added to base STF, but elasticity, stability, consistency, and temperature resistant properties of suspensions increases to a significant extent. Since the aspect ratio of nanoclays is high, it is believed that surface energy available at particle polymer interface will be more, leading to better dispersion, which would lead to an improved bonding with fibrils of high-performance fabric and efficient dissipation of energy in the event of an impact.

Interestingly, Nanomer clay as a nano-additive reduces the difference between the steady-state critical viscosity and the dynamic-state critical complex viscosity which confirm the stability and consistency of the STF with impact force.

In addition, storage modulus and loss modulus both increases as frequency and concentration increases for clay as nano-additive which will make the STF suitable for high-velocity impact applications. In contrast to only using fumed silica as an additive, clay as additive increases both viscous and elastic properties. Also, clay as nano-additive shows more stability and reproducible/consistent results.

Chapter 7: A study was conducted on alumina nano-particles as nano-additives in the fumed-silica-PEG STF. Alumina is a pure oxide in contrast to clays which are alumino-silicates. The principal goal of adding alumina particles was to investigate the effect of pure oxide on shear thickening rheology. Alumina particles lead to an enhancement of shear thickening properties at very low overall particles concentration with novel dynamic shear rate properties that cannot be attained by fumed silica particles alone.

In contrast to MMT clay particles, alumina particles at a low concentration can result in an increase in critical viscosity but the viscosity remains same on increase in concentration.

Chapter 8: Till now there was no attempt made to modify the properties of the dispersion liquid. By the addition of high molecular weight PEGs as additives to base dispersion liquid which is PEG200 results in increasing the depletion forces in the resulting suspensions, where three types of additives, PEG of molecular weights 4600, 6000 and 10000 were used. The results indicates that with the molecular weight of additives increasing, the shear thickening is remarkably enhanced up to 6000 molecular weight. Further increases in molecular weight cause shear thinning. The process of enhancement was explained quantitatively by the formation of large particle clusters. The depletion force increase with the increase in molecular weight which is favorable for the aggregation of particles in the shear thickening region. While long chains of polymer can interconnect various particles, which act as multifunctional cross-links. Interestingly, the results support the postulation that the process of alignment in these systems originates from the coupling between the polymer and the silica particles mediated by high shear flow and satisfactorily demonstrates the effect of bridging on the dynamics and strength of these STF. Furthermore, the study demonstrates that high molecular weight PEGs at high concentration results in flocculation or gel-like structure due to less number of hydrogen bonds resulting in weak interactions and shear thinning behavior. Thus, PEGs with a high molecular weight between 4600 and 6000, under some limitations, can be used as additives for increasing shear thickening behavior.

Chapter 9: Herein a study was undertaken for choosing silicone oil along with PEG or replacing some concentration of PEG with silicone oil as a dispersion liquid for improving shear thickening properties. Also, the rheology of STF with silicone oil of different viscosity has been studied in detail.

Steady-state results proved that although PEG forms hydrocluster due to polymer bridging between the particles, silicone oil due to its more branched structure results in the large hydroclusters similar to those formed in absence of it but typically at much lower particle concentration, which leads to a high extent of shear thickening as the concentration of silicone oil increases. However, for more than 20% of PEG replaced by silicone oil (100cst), shear thickening decreases possibly due to less amount of PEG which cannot modify hydrophobic silicone oil for bridging purpose. Addition of 20% silicone oil to PEG/fumed silica STF results in a tremendous increase (about 300%) in the critical viscosity and significantly only 40% decrease in critical shear rate when compared with base STF.

At high temperatures (45^0 and 55^0C), the critical viscosity drops to very low values. Thus, in general, a single STF material developed may not find application overall temperature range.

A large value of both the moduli is obtained as the frequency of oscillation increases which suggests that the suspension would be capable of showing shear thickening under a high-velocity impact.

10% of 500cst silicone oil as a suspension medium in STF is more stable than 1000cst at both high and low temperatures. 15% of silicone oil shows more instability at low and high temperatures, and this instability further increases for 1000cst silicone oil. 1000cst shows gel (shear thinning) like behavior at even a slightly higher temperature of 35^0C. Thus it was concluded that silicone oil up to the viscosity of 500cst with PEG200 as the liquid medium would result in more stable STF.

Chapter 10: The rheological properties of hydrophilic and hydrophobic fumed silica in polyethylene glycol (PEG) and polypropylene glycol (PPG) have been reported in this chapter with an explanation of gel formation. The effect of temperature was also looked at and the role of hydrophilicity was analyzed in detail. The STF consisting of hydrophobic fumed silica in polypropylene glycol that shear thickens at very low values of critical shear rate would be used for sensitive applications such as low impact or acoustic dampening situations whilst the STF consisting of hydrophilic fumed silica and polypropylene glycol that shear thickens at higher critical shear rate values can be favorably used in high impact situations such as ballistic impacts.

Chapter 11: It discusses the summary and significant findings of the present study which are also presented in a tabular form (Tables 1, 2 and 3) along with the future scope of the work.

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Chapter 2 Literature review

2.1 Background

The STF is a non-Newtonian stabilized colloidal suspension of a specific type for which viscosity increases dramatically under the high shear rate and behaves like a solid. However, when impact stress is removed, STF changes to an easy flowing liquid-like state. Thus shear thickening behavior is reversible [1]. The STF consists of hard metal oxide particles suspended in a liquid base. General examples of STF are silica particles suspended in ethylene glycol or PEG [1, 2], kaolin clay particles in glycerol [3], polymethyl methacrylate (PMMA) suspended in PEG [4] and fumed silica particles dispersed in propylene glycol (PPG) [5].

2.2 Shear thickening theories

Two main origins of reversible shear thickening suggested by researchers are the "order-disorder transition" and the "hydrocluster mechanism". Hoffman investigated the concentrated monodisperse suspensions [6, 7] and proposed that at low shear rates, repulsion and attraction forces between the particles associate with the forces of shear field and manifests in to two dimensional hexagonally packed layers. When the stress is applied the liquid medium lubricates the motion of one particle past another and the excessive stress is transmitted from one atom to the neighboring ones. Finally, instability in flow is reached after a critical value of stress. High shear stress overcomes the forces which hold particles together thus destroying the dense packing of the particles and the material expands slightly or “dilates” and the voidage between the particles increases. The liquid in this case, would not be sufficient to lubricate the flow and enable the movement of particles passing other particles. Due to this fluctuation, the ordered layers are broken down and particles jam into one another resulting in an increase in the viscosity of the fluid. Owing to this behavior, the suspensions are termed as “dilatant fluids”. Simultaneously, many suspensions such as starch pastes do not undergo dilation, thus, the term used is “shear thickening fluids”. Consequently, the transition from ordered layers of particles to the disordered state is represented as *“order-disorder transition”* (ODT) theory. This theory involves the interparticle interactions and hydrodynamic forces between the material and the continuous phase of STF.

At equilibrium conditions, the structure of the STF is only affected by the interparticle forces which are Brownian and electrostatic. However, at low shear rates both interparticle and hydrodynamic lubrication forces are effective where, the interparticle interactions allow the particles passing each other easily. As the shear rate is increased, hydrodynamic forces dominate all the other forces, the particles in STF bound together and "hydroclusters," are formed which are shear-induced transient aggregates, causing difficulty of particles to flow around each other and dramatically increase the viscosity of the fluid and rate of energy dissipation. This phenomenon is called as hydrocluster mechanism.

It was noted in several studies that both events may occur simultaneously under certain conditions, that is the disordering of layer structure of particles can be caused by the clustering [5] but Qiu-mei *et al.,*2006 [1], suggested that suspension or system cannot be explained by the ODT theory as the TEM image of silica aggregates before shear thickening have irregular shapes and thus preferred theory is clustering theory. Support for the hydrocluster mechanism has been demonstrated through rheological, flow- SANS and rheo-optics experiments [8, 9], along with computer simulation.

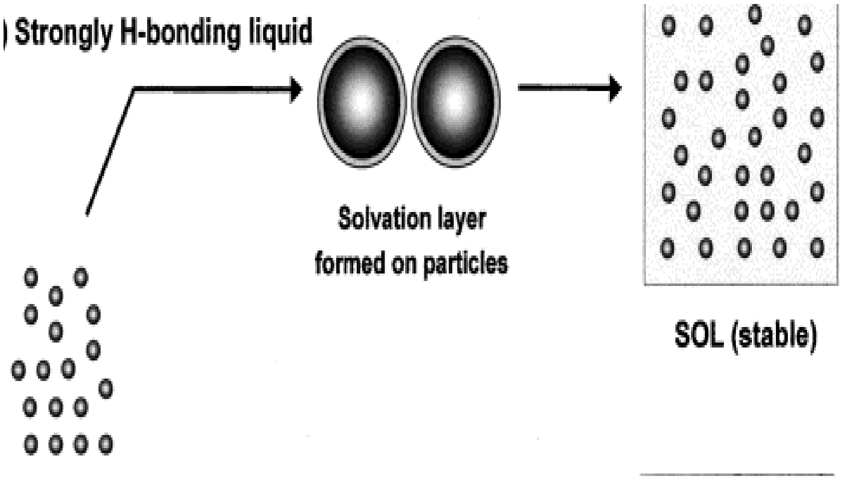

Figure 2.1 Silica particles dispersed in PEG [10]

For STF of fumed silica nanoparticles dispersed in PEG, under zero shear conditions, the molecules of PEG are absorbed on the surface of the nano-particles by hydrogen bonding between hydrogen groups of PEG molecules and silanol groups present on the surface of fumed silica particles resulting in the formation of a solvation layer around the fumed silica nanoparticles (Figure 2.1). This hinders the interaction between particles resulting in a stable suspension of STF [11, 12]. The shear rate after which increase in viscosity starts is known as **critical shear rate** and the maximum value of viscosity that is achieved by a particular STF is called **critical viscosity**. Thus, the determination of critical shear rate values is an essential parameter for liquid body armor applications in order to predict the range of the operation.

Thus, the STF respond against impact by activating a hydrocluster transition that increases the viscosity of the fluid dissipating the impact energy without any critical damage generation.

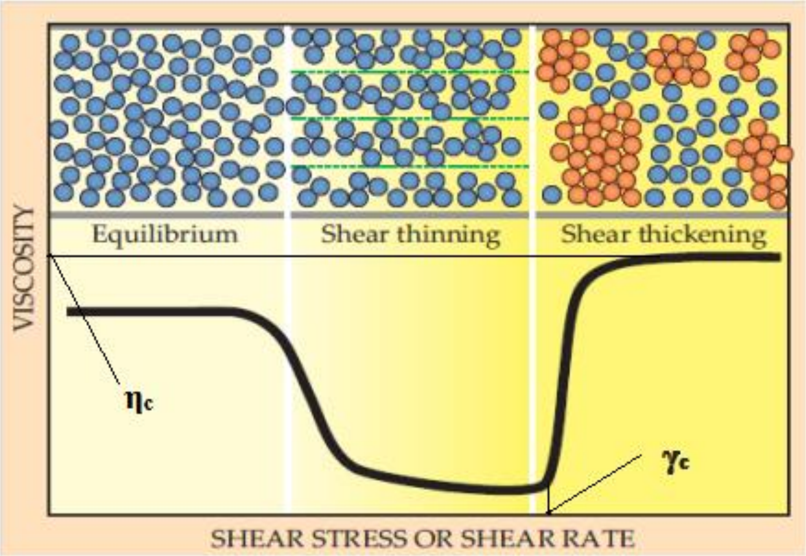

Figure 2.2 The change in the microstructure of the STF [9]

Figure 2.2 explains the change in the microstructure of the STF when STF is subjected to zero or low shear rate, the repulsive attractions between particles due to solvation layer formed around the particles create a layered structure. This layered structure effectively allows the particles to flow through the liquid medium, reducing the viscosity of the STF. Above critical shear rate, the repulsive forces are overcome by shear forces removing the solvation layer resulting in disordering of the equilibrium state and formation of hydroclusters, increasing the viscosity. However, as the shear rate increases further, the hydrodynamic force is not sufficient to bear the external force so silica particles starts to slip and the hydroclusters collapse causing a decrease in the viscosity. After removal of shear stress, the particles are again separated to form a stable suspension.

2.3 Rheological properties

The studies have focused on determining the rheological properties of STF under both steady-state shear and dynamic-state shear flow. Under the steady-state shear rate sweeps, STF show a sharp increase in viscosity values at a critical shear rate [5]. The critical shear rate depends on the volume fraction of particles i.e., higher the volume fraction, smaller the critical shear rate [12]. Under oscillatory shear [13], dynamic rheological properties reflect strain thickening behavior where dynamic parameters are measured. Steady-state rheology shows that clusters leading to shear thickening behavior are unstable and will disperse and decompose into the liquid phase PEG again after the shear stress is decreased indicating a reversible nature [1, 2]. Rheological measurements indicate that throughout the range of stress studied, loss or viscous modulus which is energy dissipated, is larger than the storage or elastic modulus that indicates the energy stored, and both strongly depend on stress [12].

The dynamic-state (oscillatory) experiments are the most suitable rheological experiments used to investigate the microstructural changes resulting from the applied stress or strain [11, 14]. In order to study the viscoelastic properties of STF, the effect of increasing stress/strain on the values of complex viscosity η^*, storage modulus G' and loss modulus G'' at a constant value of frequency have been studied. An oscillatory (sinusoidal) deformation (strain or stress) is applied to the STF and the response (strain or stress) is measured.

2.4 Factors affecting shear thickening

Many researchers have studied about the properties of the dispersed phase (particles) favorable for shear thickening behavior along with the importance of hydrogen bonds, polarity, and stability of the dispersed medium [15]. Factors on which the rheological properties of STF depend are generally divided in to three main categories: particle (size distribution, shape, solid volume fraction and interaction with each other), suspending medium (viscosity, molecular weight) and flow fields (rate and time of flow deformation, types) [16, 9].

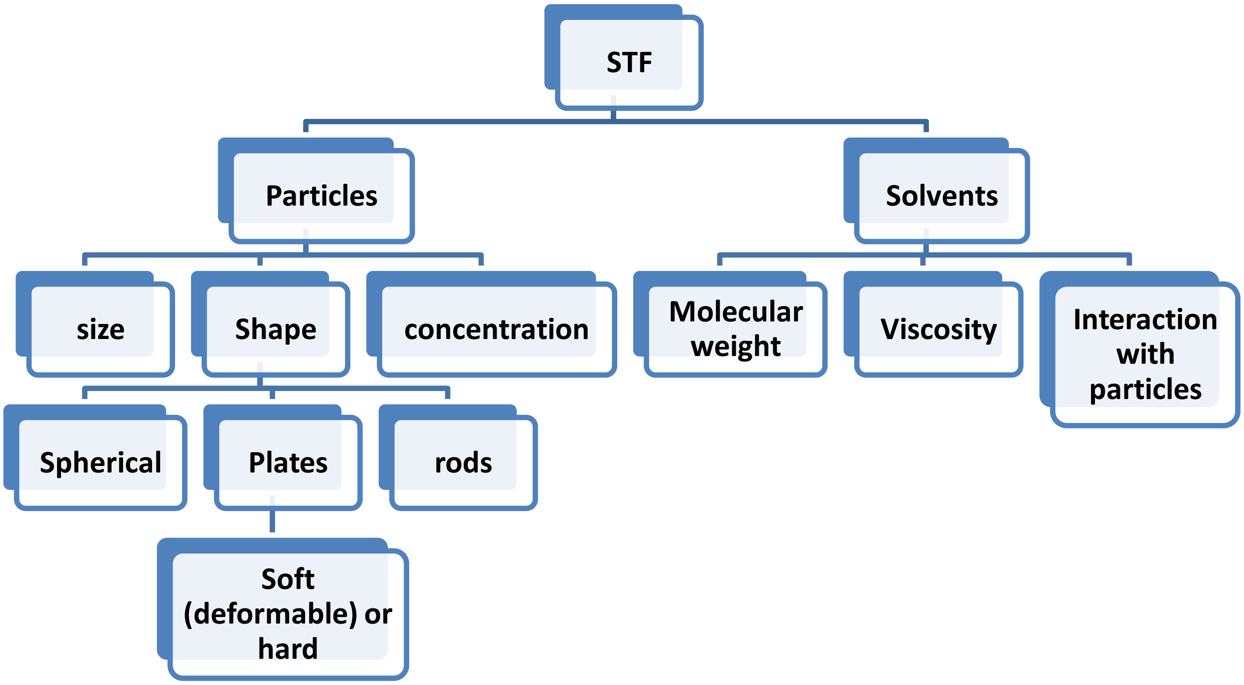

Figure 2.3 Properties of materials relevant to the rheology of STF

It should be distinguished that a certain minimum value of the **volume fraction** of silica particle is required to obtain the shear thickening behavior [17].

Mostly the suspensions with shear thickening behavior have high volume fraction >30% but studies by Qiu-mei et.al, 2008 [1], Raghvan et.al 1997 [5] and Brown et.al, 2011 [17] indicated that for fumed silica (12 nm) particles of mass fraction 9-10% i.e very low volume fraction (Φ_s), yet the shear thickening behavior takes place. This contradiction could be explained by assuming that a large amount of liquid is being congested in the loosely packed silica aggregates and the complete structure is deformed into a single entity, that increases the effective volume fraction (Φ_{eff}) much over (Φ_s).

Another important factor is **particle shape [19]**. It is found that the shear thickening properties of suspension with rod-shaped particles is greater than that of spheres, grains, and plates. Primary structure of fractal fumed silica particles consists of branched aggregates (300-400 nm), formed by the binding of primary spherical particles (12 nm) whereas sphere silica (400-500 nm) does not form aggregates. Hence fumed silica leads to a substantial increase in the viscosity of the STF at low shear rates and show gel-like behavior in non-homogeneous suspension [2]. Rosen *et al.* [3] compared STF of flat kaolin particles with glycerol and STF of spherical silica particles. Kaolin-STF shows a continuous shear thickening behavior whereas silica STF exhibits a discontinuous shear thickening rheology.

Another factor, the **particle size**, has the direct effect on the onset of shear thickening. Maranzano *et al.*,2001 [9], studied that with increasing particle size in dense colloidal suspensions, the flow curves or the critical shear rate of STF systematically shift to lower applied shear stresses. Also, it was confirmed and showed that critical shear stress values scales inversely with particle size cubed. However, contradictory results have been given by Idzkowska *et al.*,2013 [20] i.e. the critical shear rate shifts to lower values by replacing the 50 vol% fumed silica 200 nm by fumed silica of 7 nm. These results are contradictory with previous works, which demonstrates that difference in the diameter of particles allows increasing particles volume fraction in the suspension, due to the fact that gaps between larger particles can be occupied by the particles of lower diameters.

Particle-particle interaction also affects the shear thickening phenomenon. Maranzano *et al.*,2001 [9] derived a scaling relationship between the suspension properties and critical shear stress by using a two particle force balance between the hydrodynamic compressive forces and the interparticle repulsive forces. The relationship suggests a method of controlling the shear thickening and largely supports the hydrocluster mechanism of shear thickening. It also demonstrates that electrostatic repulsion plays a major role in determining the critical shear rate value for these dispersions and also proved that shear thickening is stress controlled phenomena. Chemical structure and molecular weight of the liquid medium and interaction with particles have a meaningful impact on the shear thickening properties.

Apart from the above factors, various researchers have also found that the **hardness of particles** significantly affects the shear thickening properties. PMMA (polymethylmethacrylate) particles are softer than silica particles and STF of PMMA with PEG showed clear shear thinning at the highest shear rates in contrast to the silica-STF that exhibits a discontinuous rise in viscosity at a limiting shear rate [4]. As compared to PMMA-STF, silica-STF supports larger loads due to the difference in ultimate particle strength. PMMA-STF shows reduced performance in ballistic results also. Similar results are shown by Kaolin- glycerol STF. Under ballistic impact testing, Kaolin-STF impregnated fabrics performed better than the neat fabric but poorer than silica-STF impregnated fabrics [3]. These results indicate the importance of particle hardness in STF fabric performance.

Another important parameter that affects the viscosity and critical shear rate of STF is **temperature**. For compounding the functionality of STF, it is desired to extend the temperature range of effective shear thickening behavior. Additionally, for protective applications, the materials based on STF should maintain protection up to a suitable range in different temperature/weather conditions as well as when in contact with the human body. It is known that the rise in temperature of STF reduces shear thickening and that the high shear thickening effect is shown at low temperature. Thus, research is required to reduce the negative effect of the temperature on shear thickening performance of STF. Kang *et al.,*2011, observed that both viscosity and critical shear rate values changes with temperature because as temperature increases, the hydrodynamic force inducing shear thickening phenomenon increases as Brownian motion of silica particles in the STF increases. Thus, the performance of stab-proof products made from STF and Kevlar fabric would be changed by the environmental conditions [2, 9].

Various factors come into play depending on the particles and liquid medium used resulting in different rheological and stability behavior as deduced from various studies and explained in Figure 2.1. Therefore different proposed raw materials are studied in the present work and also tabulated in Table 2.1. Overall summary of literature is presented in Table2.2.

Table 2.1 Effect of processing parameters on critical viscosity and critical shear rate

S.No.	**Parameters**	**Critical viscosity**	**Critical shear rate**
1	Volume fraction	↑	↓
2	Particle size	↑	↓
3	Particle size distribution	↓	↑
4	Interaction between particles	↓	↑
5	Solvent molecular weight	↑	—
6	Temperature	↓	↑
7	Resting time	↑	↓

Table 2.2 Summary of a few STF studies

	Type of nanoparticle (size, nm)	Liquid medium	Weight fraction %w/w	Substrate	The focus of the research	References
1	Fumed silica (14 nm)	PPG	3-10	Kevlar	Study the dynamic and steady-state rheology of STF	Raghavan and Khan,1997 [5]
2	Fumed silica(10 nm)	PEG(300) and PPG(425)	10		Rheology of Silica Dispersions in Organic Liquids	Raghvan, 2000 [10]
3	Colloidal silica (446 nm)	EG and water	55-62		Dynamic properties of shear thickening colloidal suspensions	Lee and Wagner, 2003 [21]
4	Colloidal silica (500 nm)	PEG-200	52	Kevlar and Nylon	Investigating the stab resistance of woven composite impregnated with STF	Egres *et al.*, 2004 [22]
5	Fumed silica (12 nm)	PEG (200 and 400 g/mol)	4-9		The steady and oscillatory rheological behavior of the fumed silica suspensions in PEG	Qiu-mei *et al.*,2006 [1]
6	Fumed Silica (7 nm)	PEG	55	Kevlar	Development of Stab Resistant Body Armor through Sonic Cavitation	Mahfuz *et al.*,2006 [23]
7	Silica and poly(methyl methacrylate) (PMMA)	PEG (200 g/mol)		Kevlar	Study the effect of particle hardness on STF-fabric performance by synthesizing a model dispersion of PMMA particles	Kalman *et al.*, 2007 [4]
8	Kaolin (500 nm)	Glycerol	43	Kevlar	Investigate the shear thickening of highly loaded kaolin clay suspensions for use in protective fabrics	Rosen *et al.*, 2007 [3]
9	Fumed silica (14 nm)	EG	20,30 and 40		The rheological properties of STF and its application as a damper	Zhang *et al.*, 2008 [12]
10	Fumed silica (12 nm)	PPG400 and 2000	10-11		Static and Dynamic Yield Stresses	Rosales and Harnandez, 2009 [24]

11	Colloidal silica	PEG(400+ 4000, 6000 and 10000)	50		Rheology of Shear Thickening Fluids Based on Additives with Different Concentrations and Molecular Chain Lengths	Xu *et al.*, 2010 [25]
12	Styrene /acrylate (300 nm)	EG	58 v/v		Shear-thickening behaviour of polymer dispersions under steady and oscillatory shear	Chang *et al.*, 2011 [13]
13	Colloidal silica	PEG-400	52	Kevlar	Investigating the ballistic impact resistance of woven composite impregnated with STF	Lomakin *et al.*,2011 [26]
14	Silica (500-800 nm)	PEG+ Silane	25-40	Kevlar	Shear-thickening behavior of modified silica nanoparticles in polyethylene glycol	Yu *et al.*, 2012 [27]
15	Silica(120 nm) fumed silica (300-400 nm)	EG and PEG(200 g/mol	5-65	Kevlar	Developing an advanced stab and/or ballistic proof material composed of STF and Kevlar composite fabric	Kang *et al.*, 2012 [28]
16	Fumed silica(11 nm to 14 nm)	PEG	40	Kevlar	Optimizing the ethanol content of shear thickening fluid \fabric composites under impact loading	Kordani *et al.*,2013 [29]
17	Fumed silica (11 nm)	PEG200	15 and 20		Tuning of Rheological Performance of Shear Thickening Fluid by Using Graphene Oxide	Huang *et al.*, 2015 [30]
18	Silica particles (12 or 60 nm)	PEG400	15, 25, and 35	Twaron	Characterization of the rheological and mechanical properties of shear thickening fluid-coated Twaron® composite	Baharvandi *et al.*, 2016 [31]
19	Silica particles (100 nm)	PPG400	67.5	UHMWPE (Ultra High Molecular Weight Poly Ethylene)	Impact Response of Shear Thickening Fluid (STF) Treated High Strength Polymer Composites – Effect of STF Intercalation Method	Asija *et.al.*, 2017 [32]
20	Fumed silica (12 nm)	PEG200	27.5	Open cell polyurethane foam	On the effectiveness of incorporating shear thickening fluid with fumed silica particles in hip protectors	Haris *et.al.*, 2018 [33]

2.5 Gaps in the literature

The gaps found in the literature are as follows:

1. Studies on STF considering parameters like particles morphology, fluid properties, and temperature are still sparse.
2. Only a few STF studies reports on the dynamic properties along with steady-state properties have been reported less.
3. There is very little, if any, discussion about the stability of STF.
4. There is no report on fumed silica STF modified with nanoclay(s).
5. Modification of the suspension medium have been studied in a very limited manner.

2.6 Objectives of thesis

From the identified gaps in the literature review, the following objectives have been framed.

1. Development of shear thickening fluids with varying nanoparticle (nanosilica and nanoclay) content.
2. To optimize the contents of nanoparticles in the solvent matrix for shear thickening properties.

2.7 Closing remarks

In the last two decades, a lot of work has been reported on different sizes of silica and fumed silica used with different polymers in various concentrations for STF. Also, STF impregnation with different protective fabrics has been studied. However, to date, the influence of different additives on the shear thickening performance and stability have not been widely investigated. Also, many investigators did not consider the parameters like temperature, particle morphology, surface chemistry etc. that can control shear thickening in these systems. Based on all these considerations, the STF prepared and studied in the present study forms a complex system characterized by a bi-disperse particle system. The present study aims to fill gaps in the study of STF and reports some interesting observations on the effective shear thickening properties due to the addition of relatively inexpensive additives while trying to investigate the effect of concentration, temperature, shear rate, shear stress and frequency of oscillation.

The succeeding chapter outlines the materials and methodology used to accomplish the goal.

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Chapter 3 Materials and Methodology

From the literature review, it was gathered that the rheological response of the STF is governed by the particles within a STF and the volume fraction, size, surface chemistry and dispersion/interaction with medium liquid. Systematically by quantifying the effect of changing each variable on the rheology, STF can be manufactured to suit a particular application by simply altering the composition. Thus, in the present work, several raw materials were taken and STF were produced at a range of weight fractions. Rheological properties of STF were then systematically characterized to determine the effect of varying material properties on the resultant rheology.

The properties of STF are strongly affected by the properties of raw materials as discussed in Chapters 1 and 2. The physical as well as the chemical structure of the dispersed particles and dispersing medium results in unique rheological properties at both zero shear and high shear deformations. Some studies have reported that different particles as additives (small amounts) to STF such as Graphene oxide [1]; Multiwall carbon nanotubes [2]; and Halloysite nanotubes [3]; Cellulose fibers [4] etc. leads to an increase in shear thickening properties and shift critical viscosities values to high shear rates.

For additives to aid in enhancing shear thickening behavior would require the material that combines the particle properties with the medium liquid. A typical solution can be found in the nanoclay particles and high molecular weight (and high viscosity) polymers. There are several examples in the literature about different materials that can be employed as particles and dispersion medium to be used for STF. For this study, the raw materials used were discussed in the Chapter 1 and there source is given herein, along with the processing method of STF.

3.1 Materials

Nano silica of average particle size 400 nm was obtained from Om Laboratories, India and fumed silica of average particle size 11 nm (381276) and 7 nm (S5130) was obtained from Sigma Aldrich, India. The surface area of 11 nm fumed silica is 255 ± 15m^2g^{-1} and density is

$0.072 \pm 0.008 gcm^{-3}$ whereas for 7 nm fumed silica surface area is 395±25 m^2/g and density $0.040gcm^{-3}$. Hydrophobic fumed silica particles: (CAB-O-SIL TS 610) was obtained from Cabot India Limited. The dispersion medium, polyethylene glycol of molecular weight (PEG 200) with a density of 1.127 gml^{-1} and viscosity 43-57 cps (at 20℃), PPG425 (202304) and glycerol was also supplied by Sigma Aldrich, India. Four commercially available nanoclays: MMT (682659), Kaolin (K7375), Nanomer I.28E (682608)and Halloysite (685445) were purchased from Sigma Aldrich (India) and Closite®15A (NS6130-90-932) was procured from Nanoshell, India. Nanomer I.28Eis a bentonite clay, surface modified with 25-30 wt.% of quaternary trimethyl stearyl ammonium with cation exchange capacity (CEC) of 93.7 meq/100 g. Closite 15A is a natural MMT modified with a dimethyl dehydrogenated tallow, quaternary ammonium with CEC of 125meq/100g (bought from nanoshell). Alumina particles used are synthetic oxide (gamma) and are rod-shaped particles- about 5 nm in thickness and length of 50 nm purchased from Sigma Aldrich (product no. 544833). High molecular weights PEG; PEG4600 (373001), PEG6000 (81260) and PEG10000 (309028) and Silicone oils (polydimethylsiloxane) with viscosities 100 (10834), 500 (378399) and 1000cst (378380) (25°C) were purchased from Sigma Aldrich, India.

3.2 Processing

Various STF were processed by different morphology and properties of the particles which constitute the disperse phase and also their concentrations into the dispersion medium along with changes in the properties of dispersion medium by addition of different fluids of various molecular weight and viscosity. The steady-state and dynamic-state rheology were then evaluated by using rheology tests by the rheometer.

Firstly, the primary particles and primary liquid medium along with additives were dispersed using probe sonication method. Out of ultrasonication bath, homogenization and mechanical stirrer, probe sonication (ultrasonication probe of 6mm dia probe, power of 750W and frequency of 20 KHz) at 40% power was chosen based on its effectiveness for high surface area fumed silica particles dispersion in the liquid medium. In the second step, as-prepared STF was left for 12h vacuum oven was used to remove the bubbles trapped during sonication process then investigated by the rheometer. A brief description of the process is shown in Figure 3.1. Figure 3.2 illustrates a schematic representation of the materials and equipments used for the preparation of STF samples. It should be noted that stability of prepared STF was closely related to processing variables, in addition to its composition.

3.3 Characterization

As uniform distribution of nanoparticles is an essential condition for any meaningful and reproducible study of rheology of these systems, particle dispersion was determined through Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). For TEM analysis firstly, samples are sonicated with ethanol having twice the amount of that of the sample for 30 min and then a small drop of solution is placed onto a Cu grid and allowed to evaporate, typically under vacuum before being viewed.

3.4 Rheology

The shear thickening behavior depends on a large number and range of variables. From the application point of view a wide range of shear rate prevails as many operations (for high velocity projectiles) are characterized by high shear rates above 10^{3} sec^{-1} or higher and a few processes like damping occurs at relatively lower shear rates [5]. The dynamic rheological tests were done at 25^{0}C from which, the storage, elastic or recoverable response and dissipative, viscous or damping response of the STF could be deduced. Also dynamic tests are important because once the high speed projectile hits the STF, the initial response is by the STF in fluid state and very quickly it enters a solid like state. The former response is studied through steady-state rheology giving critical shear rates and the latter by dynamic experiments which would give critical strain. Additionally, for STF time-scale of deformation is also very important therefore, dynamic rheology at different frequencies were also probed. Earlier the most reliable strategy for morphological characterization of viscoelastic polymers through rheological measurements was based on the dynamic small amplitude oscillatory shear within the linear viscoelastic range (LVE range) [6]. But recent proposed alternative technique to characterize the liquid two-phase system morphology is based on large amplitude oscillatory shear flows [6, 7]. Also for STF high amplitude rheology will allow evaluation of properties that might otherwise be hardly possible with traditional experimental protocols. Therefore, in this study strain amplitude sweep was done for STF samples up to very high applied strain (10^{4}%). The rheological tests were done by rheometer (MCR-52) with a cone and plate geometry having a plate diameter of 40mm and a cone angle of 2^{0}. The small gap size of 0.08 mm prevents slip [8, 9]. All steady-state rheological measurements were conducted at wide range of temperatures with temperature control provided by the Peltier element inbuilt in the rheometer. Before every experiment, a protocol similar to that mentioned by Galindo-Rosales and Rubio-Hernandez [9] including a pre-shear of 0.1 to 1s^{-1} and a pre-strain of 1 to 10% for 60s followed by resting period of 120s was performed for steady-state and dynamic-state rheology, respectively. The cone and plate geometry insures that homogeneous shear conditions are maintained since the shear rate (and shear deformation) is constant in the entire conical gap. [10, 11, 12-15].

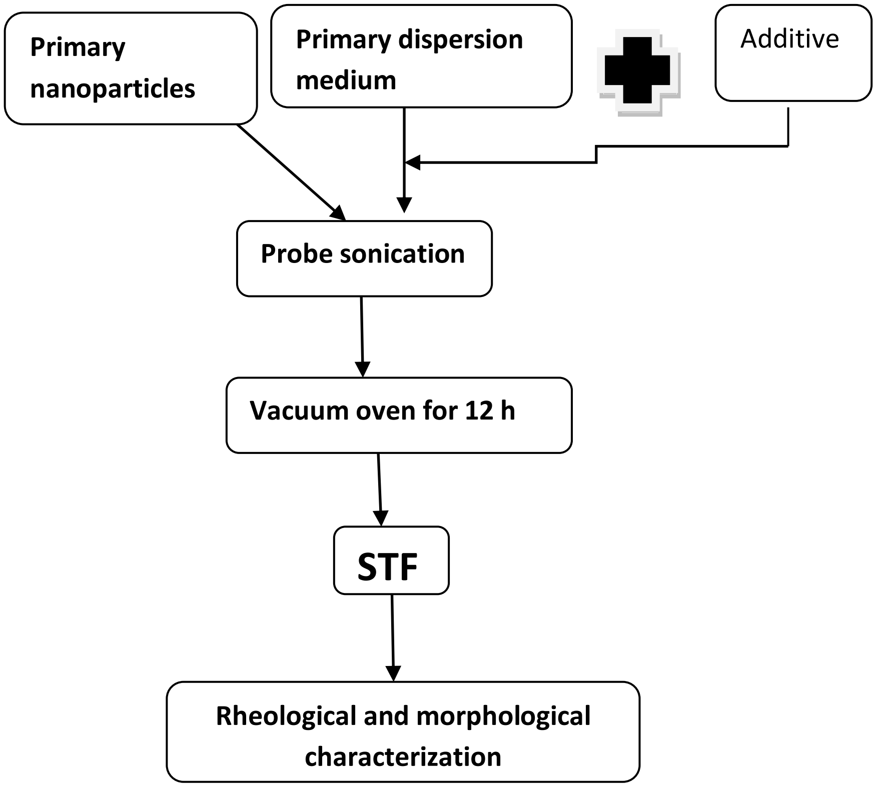

Figure 3.1 A generic procedure for STF preparation

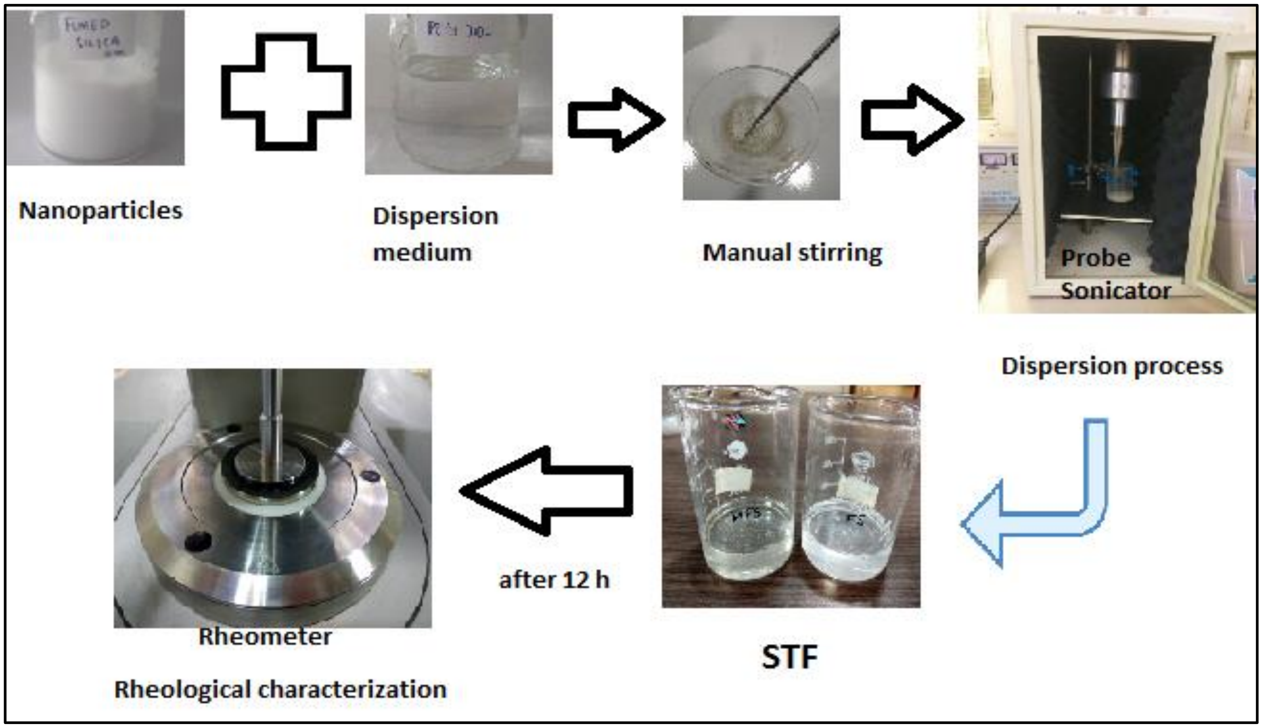

Figure 3.2 Schematic representations of the materials and equipments utilized in the preparation and study of STF

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Chapter 4 Effect of composition and processing conditions on the rheology of STF

The processing conditions for STF preparation were optimized. The STF was prepared by silica, fumed silica and clay particles as primary dispersant particles at different concentrations and steady-state rheology was studied. Additionally, the influence of clay as an additive on the rheological behavior of STF was studied.

4.1 Introduction

Among the particles and carrier fluid used for making STF, silica particles and PEG and PPG respectively, are most widely used because of high strength, high shear resistance properties of silica particles and stability, high boiling point, polarity and non-flammability properties of the carrier polymeric fluid [1-5]. However, the STF has certain limitations in terms of stability, the range of critical shear rates and critical viscosities. Thus, some additives may be helpful in tuning the shear thickening properties of STF according to the application [6]. The materials which show a certain degree of compatibility with primary silica particles and polymer fluid can be introduced as additives to alter the shear thickening properties of the silica-PEG STF. A limitation in adding additives is the flocculation of primary particles and non-uniform dispersion accompanied with a high viscosity. Therefore, the concentration of additives should be very small. In this chapter, the processing of various STF and properties of STF with different additives is being reported.

4.2 Processing

Suspensions were prepared by dispersing silica (400 nm), fumed silica (11 nm and 7 nm) and different clays as primary particles in a liquid medium PEG200 for 30 min by probe sonication. Rheological studies were conducted after removing air bubbles trapped in the samples during processing by subjecting the samples to vacuum for 12 h.

4.3 Results and Discussion

4.3.1 Silica as primary particles

Silica particles used in the present study is of 400 nm diameter (Figure 4.1). STF were made by different concentrations of silica particles to comprehend the minimum concentration at which shear thickening will take place. It was observed that no significant increase in viscosity was obtained for 54% and 60% concentration of spherical silica particles as shown in Figure 4.1a. Theoretically, 60% by weight concentration of spherical silica particle is the minimum required for the pre[parathion of STF [7, 8]. Although 66% and 68% showed a sharp increase in shear thickening behavior (Figure 4.2b) however, 70% concentration show shear thinning behavior may be due to non-homogeneous suspension.

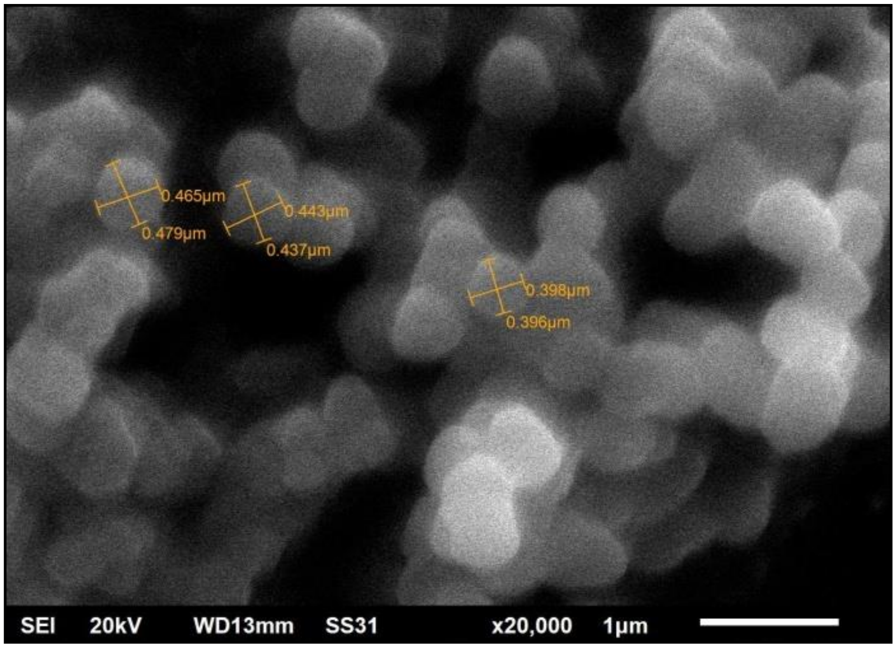
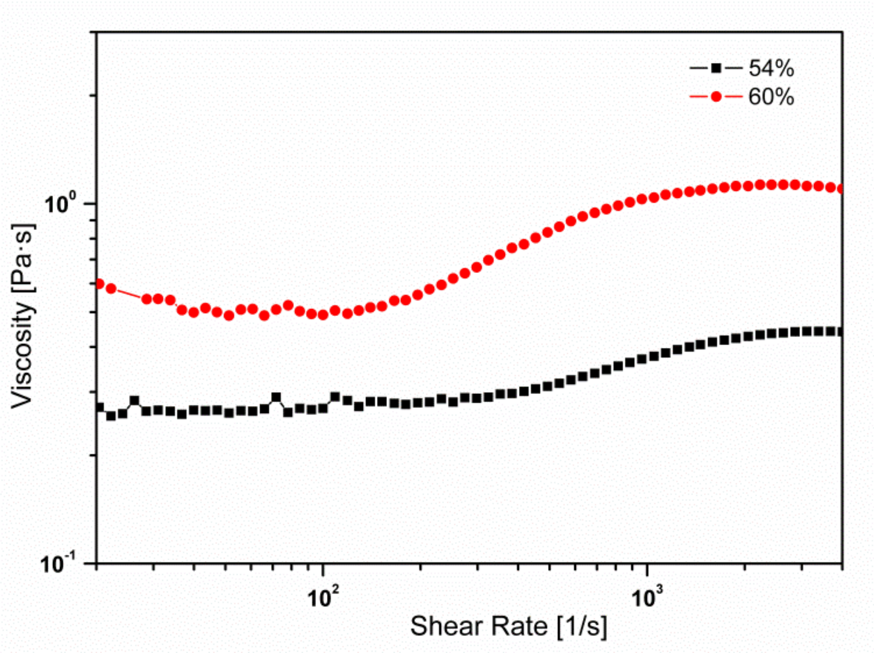
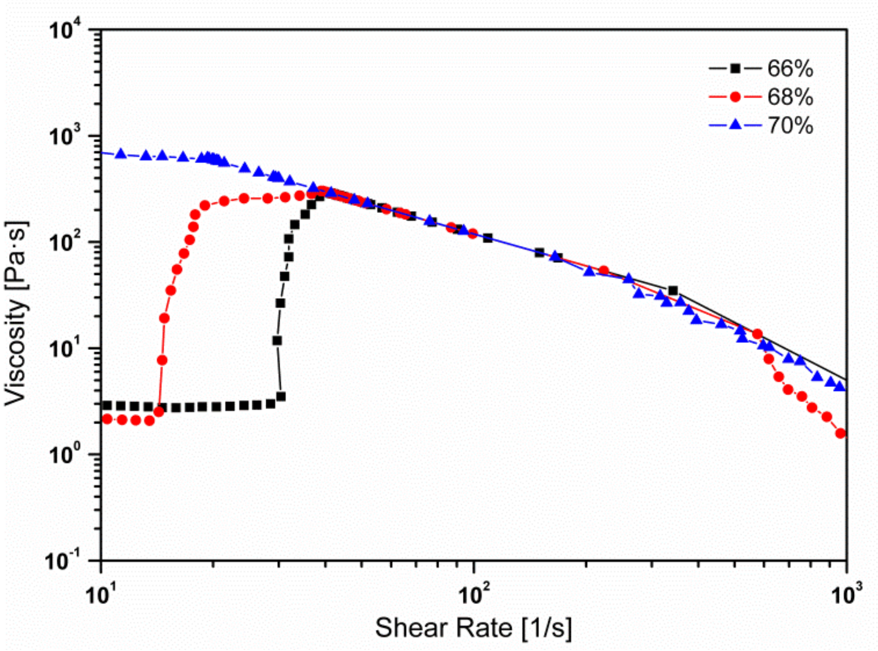


Figure 4.1 TEM image of silica particles



(a)



(b)

Figure 4.2 Effect of a) 54% and 60% b) 66%, 68% and 70% silica concentration on steady-state viscosity of STF

4.3.2. Fumed silica as primary particles with an optimum processing

Fumed silica particles used in the present study is of 11 nm diameter (Figure 4.3).

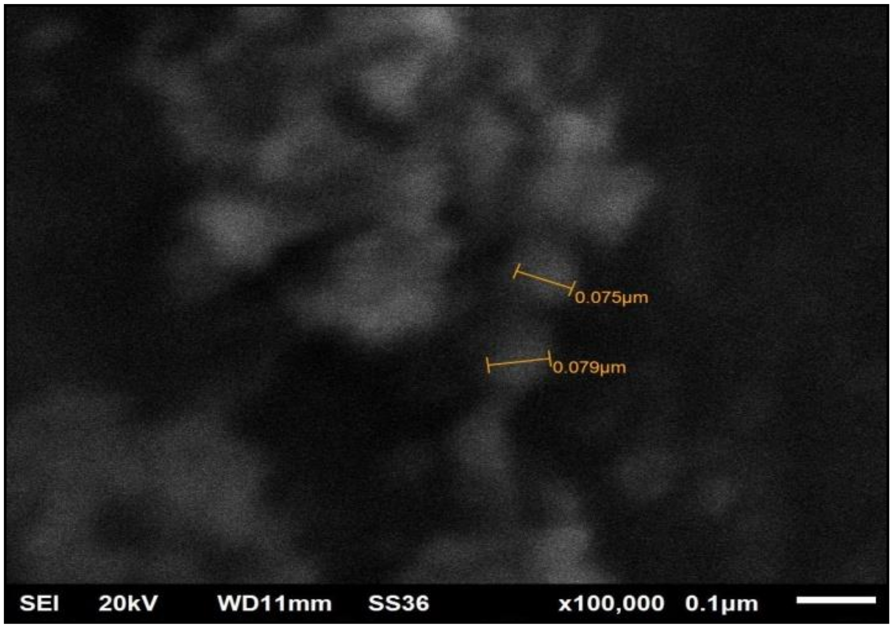


Figure 4.3 TEM image of fumed silica particles

Fumed silica is dispersed in the polymeric fluid by means of a probe sonicator. Over dispersion results when fumed silica aggregates are broken down past an optimum aggregate size. Small aggregates then become so homogeneously dispersed, that the distance between adjacent aggregates becomes large, and aggregate-to-aggregate interaction is reduced, which results in a decrease in critical viscosity at high shear rates. Thus, optimum mixing time is composition specific and must be established for each suspension.

On comparing 20% fumed silica dispersion in PEG for processing time of 30 min and 10 min (Figure 4.4), it can be concluded that viscosity increases by approximately 5 times for an optimum time of 10 min. A sonication time of 10 min was found to be just sufficient to properly disperse the particles of 20% fumed silica in PEG without showing any gel-like behavior which would occur in the case of aggregation of particles resulting in enhanced and reproducible shear thickening properties. **Therefore, if the system is sheared for a longer time (even for an additional minute) the resultant suspension can sometimes become water like with no shear**

thickening properties. This phenomenon may be explained as resulting from the breaking of particles, reducing the mean length and consequently decreasing aspect ratio, resulting in overdispersion which somehow affects its ability to form STF. Thus, only the optimally dispersed nanoparticles display a high increase in viscosity due to an increase in the surface area of suspended nanoparticles compared to agglomerated/clustered particles. This indicates that when processing shear thickening fluids with any nano-particle, processing conditions have to be arrived at with great care. In the literature also, for the same concentration and size of fumed silica particles in PEG, different critical shear rate and critical shear viscosity have been reported which may be attributed to the difference in processing parameters including different sonication time [9, 10](47. 48 of nanomer paper).

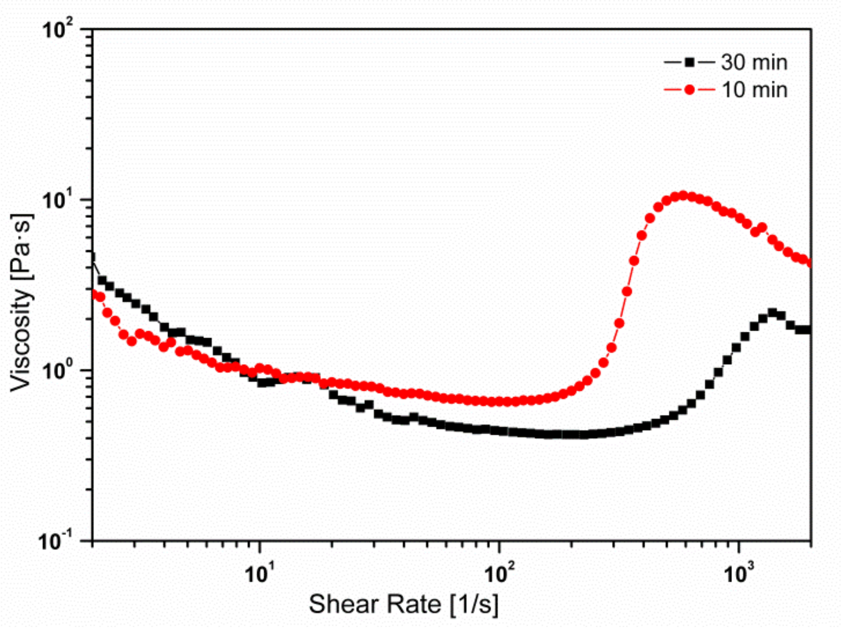


Figure 4.4 Effect of sonication time

4.3.3. Fumed-silica of different particle size and concentration as primary particles

STF was prepared by 20 weight % of 7 nm and 11 nm fumed silica and steady-state rheology was studied (Figure 4.5). It was seen that as the size increased from 7 to 11 nm, critical viscosity values increased by about 4 times (from 2.5 to 10 Pa.s) at a decrease in critical shear rate values of about only 2.5 times (i.e. 500 to 200 s^{-1}). Preliminary testing was done on the various concentrations of fumed silica in PEG200 to determine the optimum weight fraction that exhibits smooth shear thickening behavior with appreciable viscosity and large critical shear rate. For fumed silica concentration less than 20% the viscosity of the STF does not change significantly due to the reason that at low concentration the interactions between fumed silica and PEG are weak. The rheology of 22.33%, 23.08% and 23.81% i.e 3 phr (parts per hundred of resin/STF), 4 and 5 phr fumed silica in 20% fumed silica-PEG respectively, along with 23%, 26% and 29% concentration of fumed silica in PEG were studied. The effect of the increase in the concentration of fumed silica particles was studied up to the limit imposed by concomitant increase in viscosity reached to allow a better increase in shear thickening behavior. Steady-state results as shown in Figure 4.6, show that a sudden increase in viscosity takes place after a critical shear rate (due to formation of hydroclusters that results in jamming), followed by a sudden decrease for high concentration and a very gradual decrease for low concentration (due to possible breaking of hydroclusters under high shear rate). From Figure 4.6 it is noted that, as concentration increases critical shear rate decreases and viscosity drastically increases for even as low as 3% increase in the concentration. Thus, high concentration leads to an enhancement in the critical viscosity values but the concentration has to be evaluated according to the system critical viscosity as well as critical shear rate requirement. For the study in subsequent chapters, 20% concentration was chosen, as a base/reference, as it gives high enough critical viscosity with margins of adding different additives without causing flocculation or settling of particles.

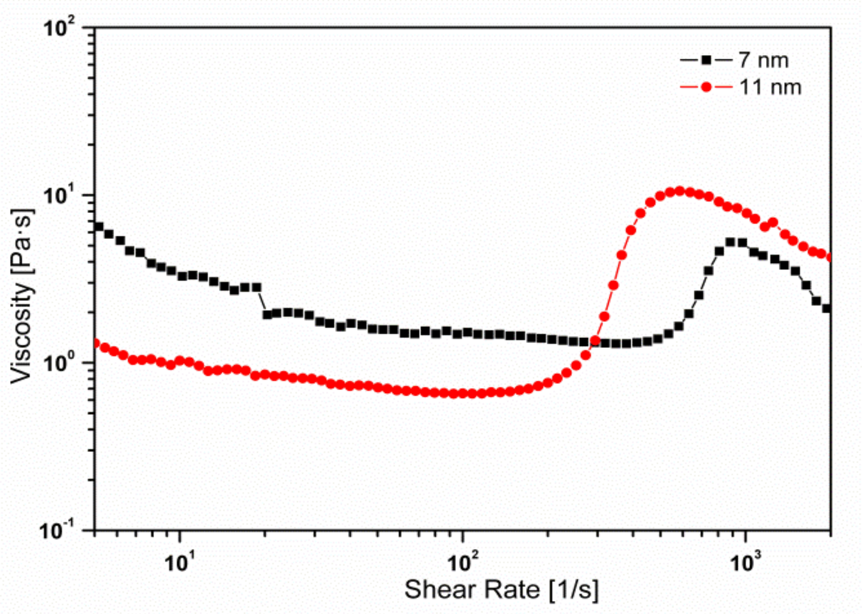


Figure 4.5 Steady-state rheology of 20% concentration of 7 nm and 11 nm fumed silica STF

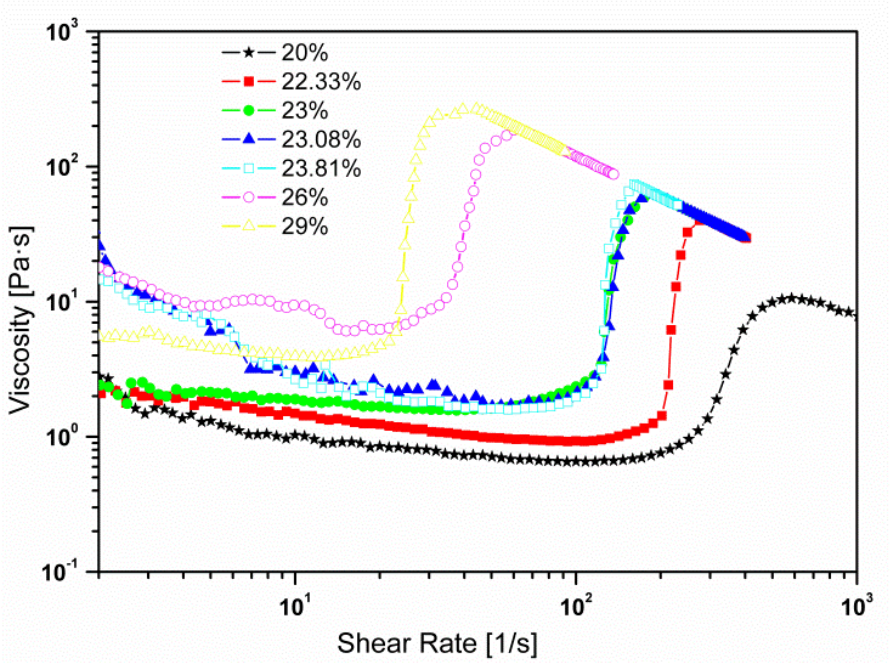


Figure 4.6 Effect of concentration of 20% fumed silica with different percentages of fumed silica (11 nm) STF

4.3.4 STF with silica and fumed silica particles

From studies of silica and fumed silica as primary particles (section 4.3.1 and 4.3.3) it can be concluded that fumed silica contributes more to critical viscosity values whereas silica particles affect comparatively more with respect to critical shear rate values. Therefore, a combination of both type of particles may enhance critical viscosity as well as critical shear rate. In fact, shear thickening effect was significantly enhanced with the addition of fumed silica as shown in Figure 4.7. This particular blend composition consisting of 25% silica, 19% fumed silica in PEG200 gives 23 s^{-1} critical shear rate and 41 Pa.s critical viscosity. An interesting observation is that size of particle being mixed can control the onset of shear thickening.

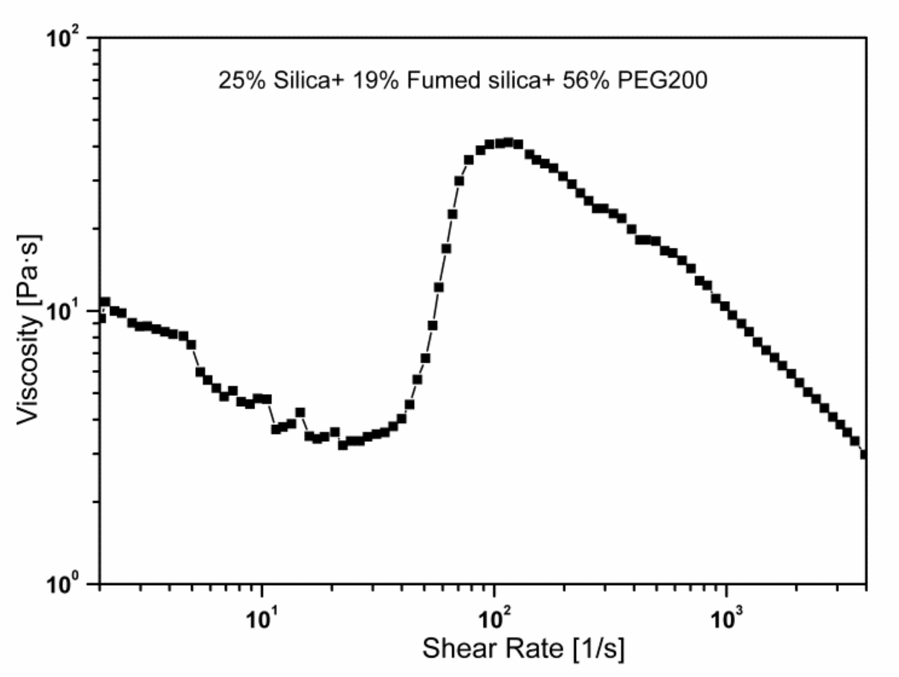


Figure 4.7 Effect of blending of silica and fumed silica

4.3.5 Nanoclays as primary particles

The dispersion of nanoclay (MMT and Kaolin) as primary particles in PEG200 is very difficult. As soon as concentration reaches more than 15%, the flowability of the suspension ceases. Out of all suspensions involving MMT and Kaolin, only Kaolin clay dispersed in glycerol showed some thickening properties but at a very small value of critical shear rate. STF of Kaolin clay as a dispersed particle in glycerol with concentration up to 63% as depicted in Figure 4.8 shows continuous shear thickening for a very narrow range of shear rate with a very low critical shear rate of 0.2 (1/s) and critical viscosity of around 40 Pa.s. MMT clay does not show thickening behavior in either PEG or glycerol. The reason may be attributed to the difference in the properties of both. MMT clay is from a group of clays called smectites which can take up extra water in their interlayers and swell whereas Kaolin are non- swelling clays as they consist of many aggregately strong hydrogen bonds that do not expand or swell. Table 4.1 summarizes some of the dispersions in which shear thickening was not observed. The results indicate that even at high concentrations, clay particles dispersed in PEG do not show shear thickening behavior which again indicates the important point that clay particles can be possibly used only as an additive as secondary particles (in small concentration due to reduced processibility for high viscosity suspensions) along with primary particles for tunning shear thickening properties to a significant extent, and at considerable savings.

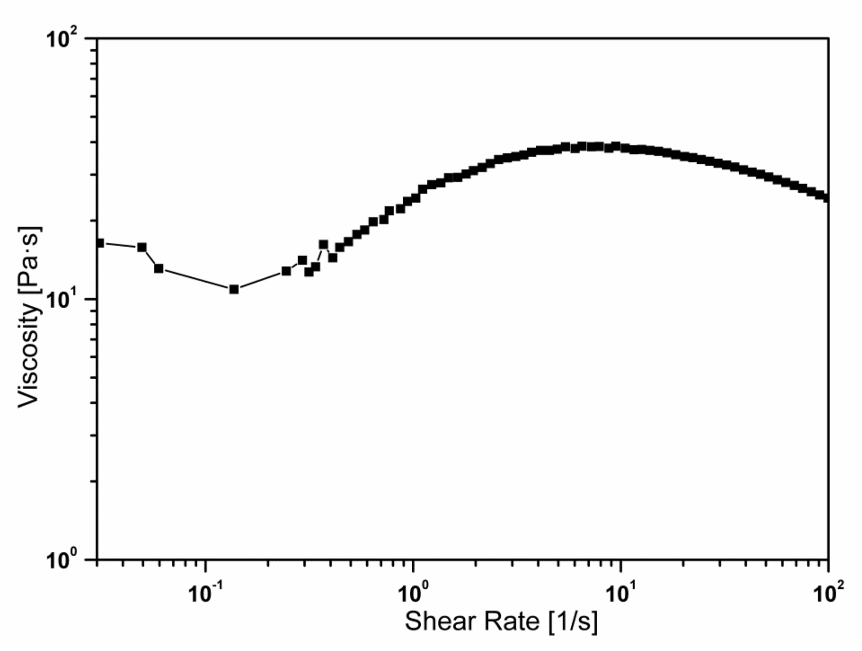


Figure 4.8 63 % Kaolin clay and glycerol STF

Table 4.1 Compositions of clay/liquid in which shear thickening behavior was not observed

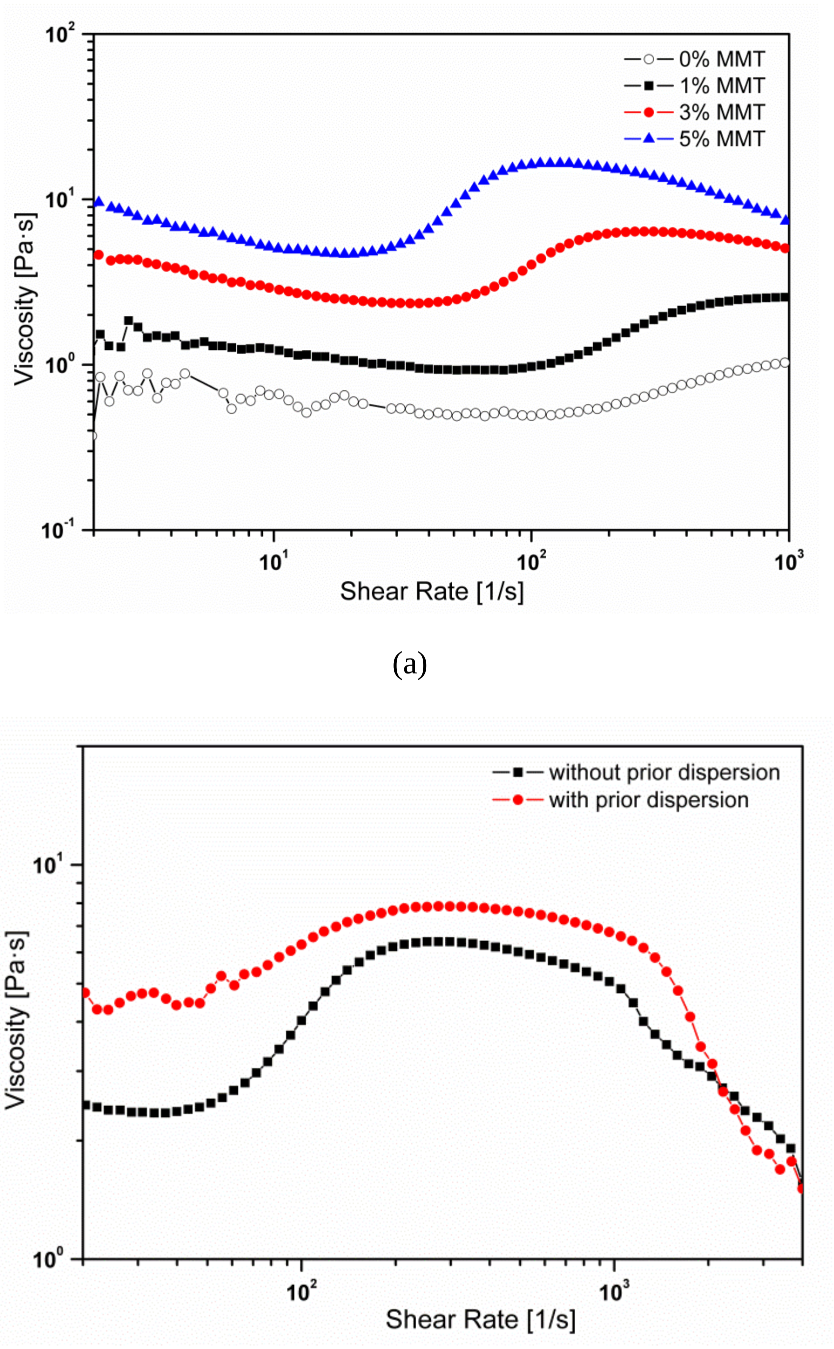
Suspension	Composition (w/w)
OMMT clay (Closite®15A)+PEG200	65
MMT clay+PEG200	45
MMT clay+Glycerol	45
Kaolin clay+PEG200	47
Nanomer clay+PEG200	35

4.3.6 STF with clay particles as additives

As 60% silica-PEG STF showed smooth shear thickening with low values of viscosity (Figure 4.2), and it was chosen as an optimum concentration for studying the effect of additional MMT clay as secondary particles. The different concentrations of MMT clay (1, 3 and 5 phr) were added into the 60% STF as shown in Figure 4.9a. The highest maximum viscosity was obtained for 5% of MMT clay (Figure 4.9a). However, an important observation as shown in Figure 4.9b is that critical viscosity increases significantly on a prior dispersion of clay (3 phr) in PEG for 2 min sonication before addition of 60% of silica particles. This indicates that clay addition in prepared STF after all silica is added in PEG would not result in proper dispersion of clay particles resulting in an overall decrease in critical viscosity values. Therefore, a different method of processing STF with additives must be followed. Firstly, clay particles (additives) should be dispersed/exfoliated in the liquid medium (PEG). Then, the primary silica particles should be added.

4.3.7 Effect of temperature on fumed silica STF

As STF are very much sensitive to temperature, therefore, temperature during sonication should also be monitored [11]. If the temperature at the time of processing will increase, it will lead to enhance shear thinning. Thus, the temperature during probe sonication was maintained at 25^0C.



(a)

(b)

Figure 4.9 a) Effect of addition of MMT nanoclay in 60% silica STF b) Effect of dispersion of nanoclay in PEG prior to addition of nanosilica

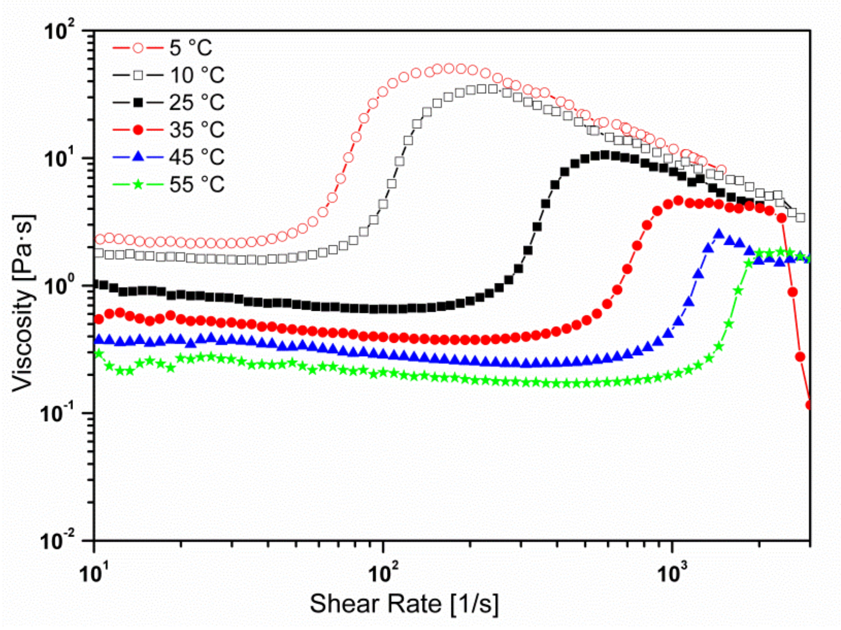


Figure 4.10 Effect of temperature on 20% fumed silica STF

Also, the rheological studies of 20% fumed silica STF at different temperatures were done and are shown in Figure 4.10. It is evident that as temperature increases, the strength of hydrogen bonding between the particles and PEG molecules decreases resulting in a decrease in low critical shear viscosity. Also with an increase in temperature, Brownian forces and repulsive forces increases which results in the requirement of a large shear rate for formation of hydroclusters. Therefore, on increasing temperature, critical viscosity decreases and critical shear rate increases.

4.3.8 Stability

Protective materials incorporating STF must maintain their properties for a long time. The durability of STF depends on the durability of individual components. Time stability of the STF is thus another important issue. Wang and Wunder (2000) and Gunko *et.al.* (2005) observed that nanoparticles of less particle size have a significant effect on the thickening properties of STF as an aggregation of primary particles increases with an increase in specific surface area. Thus, chances of gel-like behavior increases for smaller particles characterize by constantly shear thinning rheological response [12, 13]. Additionally, as concentration increases STF performance trends more to gel-like behavior. Fumed silica (11 nm) suspensions are stable

(Figure 4.11b) for more than 1 month since no sedimentation was visually observed but the nanosilica (400 nm) suspension (Figure 4.11a) did show phase separation after one month. Also for 7 nm fumed silica gel-like structure can be seen after one week (Figure 4.11c). Thus, fumed silica particles of 11 nm diameter were taken up for further studies.

Figure 4.11 STF of a) 60% of 400 nm silica particles b) 20% of 11 nm fumed silica particles and c) 20% of 7 nm fumed silica particles

4.3.9 Properties for an optimum STF

As stated earlier (Tables 2.1 and 2.2) attempt was made to carefully study the report in literature [14-17] and correlate properties of STF as a function of composition and processing parameters, it is desirable that STF should have a high value of critical viscosity at high values of critical shear rate. High values of critical viscosity are required so that when subjected to shear STF can show high shear resistance properties similar to solid. A large value of critical shear rate is important so that STF can be liquid or in low viscosity state at normal shear stress or movement of the wearer to provide flexibility whereas at high shear rates such as found in ballistics, it should show shear resisting properties protecting the wearer.

4.4 Conclusion

It can be seen that although the morphologies of both primary silica particles are different, the trend of each rheological profile is basically same i.e. with an increase in shear rate values, viscosity first decreases and then after critical shear rate value the viscosity begins to increase rapidly. At higher shear rates, the viscosity begins to decrease after achieving a critical viscosity value. Simple silica particles compared with fumed silica particles require greater particle concentration for appreciable shear thickening. Thus in addition to being comparatively much expensive, the silica particle STF would have higher density and adversely contribute to the weight of the fabric incorporating silica STF. Optimum mixing time and temperature are composition specific and must be established for each formulation.

The presence of clay as secondary particles improved rheological properties, increasing the shear thickening behavior. Nano-dispersion of clay particles in PEG before addition of silica particles is very important for enhancing shear thickening particles.

Kaolin clay forms STF with glycerol whereas MMT clay alone was not observed to form STF. This may be due to the fact that MMT can take up extra water in their interlayer and swell whereas Kaolin are non- swelling clays as they consist of many aggregately strong hydrogen bonds that do not expand or swell.

20% by weight fumed silica particles provided an optimum combination of relatively low viscosity at zero – shear, marked shear thickening, high- post-transition viscosity and also ease of dispersion and relative stability with the consistency of results. ***For this reason, 20% concentration of silica-PEG STF was selected as a base for all studies as given in subsequent chapters.***

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Chapter 5 Various nanoclays as additives

As observed in the previous chapter that clay particles can be used to modify shear thickening properties, a comparative study of the rheology of the base/reference shear thickening fluid (STF) of 20% fumed silica in polyethylene glycol (PEG200) with different nanoclays as additives have been reported in this chapter. The nanoclays used are montmorillonite (MMT), Closite®15A, Kaolin and Halloysite clay. The objective was to study the effect of relatively cost-effective clays as a partial substitute of nano fumed silica particles. Specifically, the effect of type and concentration of the clay along with temperature and frequency were considered.

This study is based on: Effect of addition of different nano-clays on the fumed silica-polyethylene glycol based shear-thickening fluids ; Mansi Singh, Rajeev Mehta, Sanjeev K Verma and Ipsita Biswas; Materials Research Express ; DOI: 10.1088/2053-1591/aa9f3f

5.1 Introduction

It is reported in literature that clay particles increase the material strength of many composites and only a concentration of <5 weight % of clay can be fully exfoliated for improved properties in polymer nanocomposite [1]. Also, seen in the previous chapter that Kaolin clay naturally exhibit some shear thickening properties [2]. Additionally, surface modification of clay by ion exchange can make them compatibilized with a wide variety of matrix polymers due to the generation of an organophilic surface [3, 4]. At the same time, the process helps to separate the clay platelets so that they can be more easily intercalated and exfoliated in liquid medium i.e the layers no longer lie opposite to one another, but randomly ordered, separated with polymer chains in the STF system [5].

It is also envisaged that the use of nanoparticles with different morphology (e.g. nanotubes) might provide additional benefits in polymer nanocomposites which are not possible with typical MMT and Kaolin clays [6-10]. Thus for both modified clay (Closite®15A) and tubular shape (Halloysite) particles effective volume fraction would decrease and relatively enhanced properties would be obtained at low concentrations. With superior properties and relatively low-cost clay as an additive in fumed silica-PEG200 STF would be an important step in STF development. Thus in this chapter, the effect of commercially available nanoclays on the rheological behavior of the STF has been investigated. Besides, it has been reported that the structural and mechanical properties of clay along with swelling properties play an important role in composites [11].

5.2 Processing

Fumed silica and nanoclay were dried in an oven for 1h. 0.75/1.25 g of nanoclay was dispersed in PEG200 for 5 min using sonication (ultrasonication probe, 40W, 6mm diameter probe) as exfoliation of clay is a prerequisite requirement [12-14]. 5 g of fumed silica was then dispersed in 20 gm of PEG for 10 min. Rheological studies were conducted after removing air bubbles trapped in the samples during processing by subjecting the samples to vacuum for 12 h. All the concentrations are given in phr (parts per hundred of resin/STF). Different loadings of clay particles i.e 2.9 and 4.76 weight % (3 and 5 phr) in base STF were studied.

5.3 Results and discussion

5.3.1 Characterization

The SEM micrographs presented in Figure 5.1 shows the phenomena of agglomeration happened in the nanoscale and platy structure of clay materials with different sizes gluing together. MMT and Kaolin clays show plates like structures while Halloysite clay shows tubular-like structures.

TEM of the prepared STF samples was used for surveying the state of dispersion of nanoparticles in the solvent. The interaction of Halloysite particles with fumed silica particles was analyzed using TEM (Figure 5.2). In the STF of fumed silica with Halloysite, on the other hand, the fumed silica nanoparticles covering the surface of Halloysite particles is seen which is due to the hydrogen bonding between hydroxyl groups present on the surface of silica particles with those of Halloysite particles.

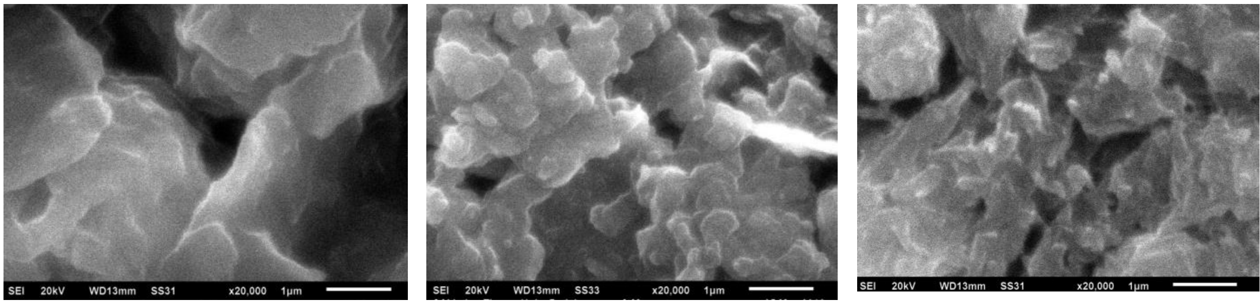


Figure 5.1 TEM images of a) MMT, b) Kaolin and c) Halloysite clay

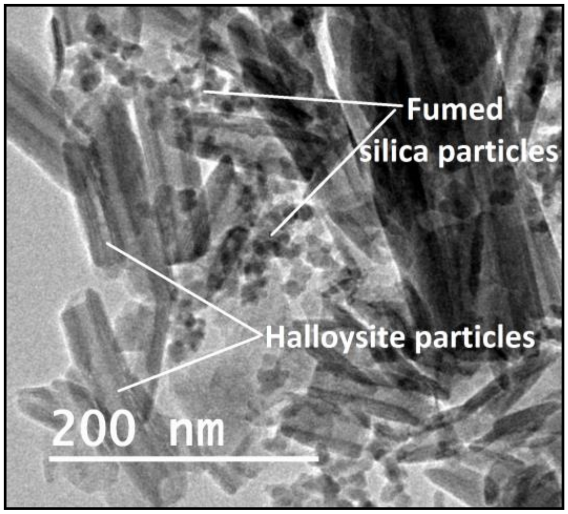


Figure 5.2 TEM analysis of base STF with 3 phr halloysite as the additive

5.3.2 Rheology

5.3.2.1 Steady-state rheology

The steady-state viscosity profiles of STF with a concentration of 3 and 5 phr additives along with 20% fumed silica-PEG STF at 25^0C are shown in Figure 5.3. It was found that less than 3 phr concentration of clay show very less increase in shear thickening properties compared to reference STF and concentration of clay more than 5 phr sometimes leads to aggregates during processing or gels on storage for several days. STF with additives largely increases the critical value of viscosity compared to pure fumed silica-PEG STF. This confirms that clay particles contribute in some way to the strength of the shear thickening response (accompanied by a decrease in the critical shear rate) with the increase in particle loading from 3 to 5 phr. Moreover, the addition of clay reduces the tendency of fumed silica to flocculate therefore initially viscosity is low. At high shear, the attractive forces become dominant where due to movement of colloidal particles and presence of clay particles, hydrodynamic forces increases resulting in high shear thickening properties. This is attributed to the entanglements of silica particles with clay particles, thus, decreasing the inter-particle distance of silica particles resulting in hydroclusters formation at low shear rates.

The rheology also reveals that for both ion modified (Closite®15A) and rod-shaped (Halloysite) clays there is an increase in viscosity for both 3 and 5 phr concentration with the 5 phr composition depicting higher and steeper viscosity profile. This behavior may be due to the fact that the specific gravity of the clay reduces after modification and tubular shape of clay increases surface area of contact with the liquid polymer. Thus for both modified and tubular shape particles effective volume fraction decreases and relatively high shear thickening is obtained at low concentrations.

MMT as additive shows very little change in viscosity, along with a broad shoulder (large range of shear rates for shear thickening behavior). The 3 phr concentration of Kaolin and Halloysite clay also show a broad shoulder. However, Closite®15A show a steep rise in viscosity values. This can be correlated to the observation shown by Bergenholtz [15], that the greater shear thickening microstructure or hydrocluster distortion is exhibited by the charge stabilized particles [16, 17]. As ion exchange has made Closite®15A particles charged stabilized which has increased the interparticle repulsive forces and Closite®15A as additive show small range of shear rates for shear thickening as compared to charge neutralized Kaolin, MMT, and Halloysite.

Thus, it is concluded that volume fraction is largely connected with particles size and properties as these can change the electrostatic interactions, leading to a different range of interactions in the system.

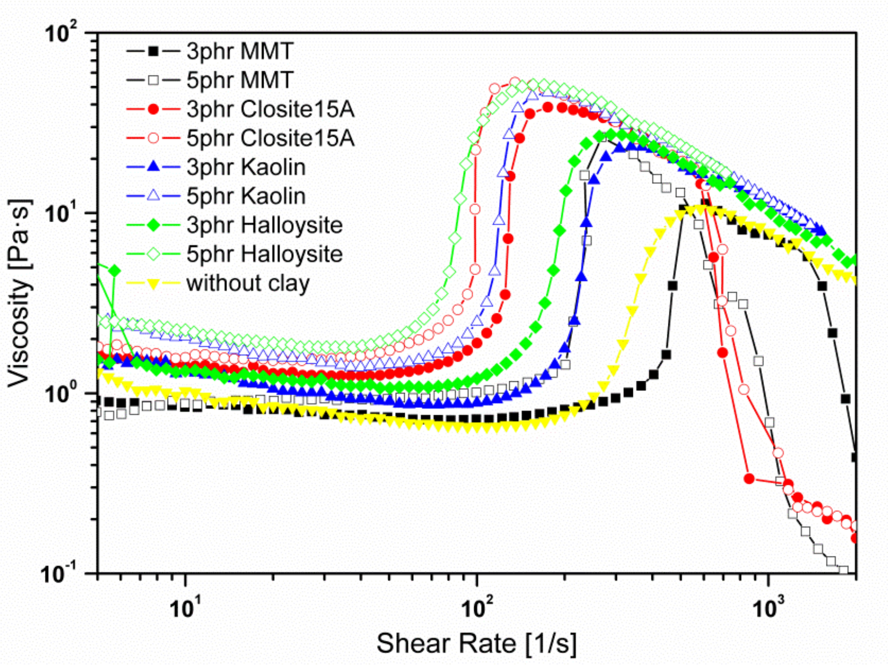
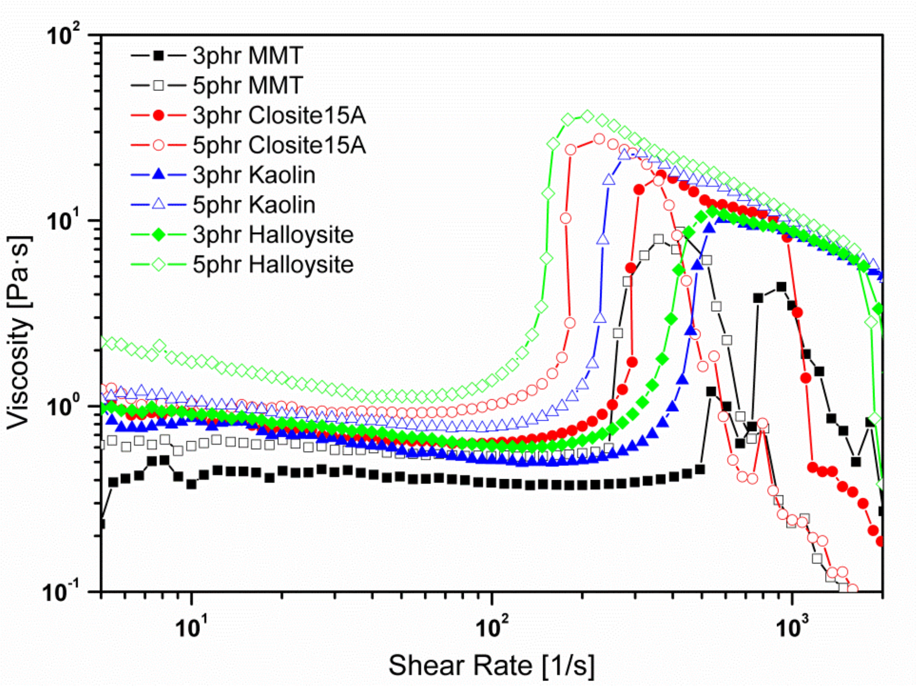
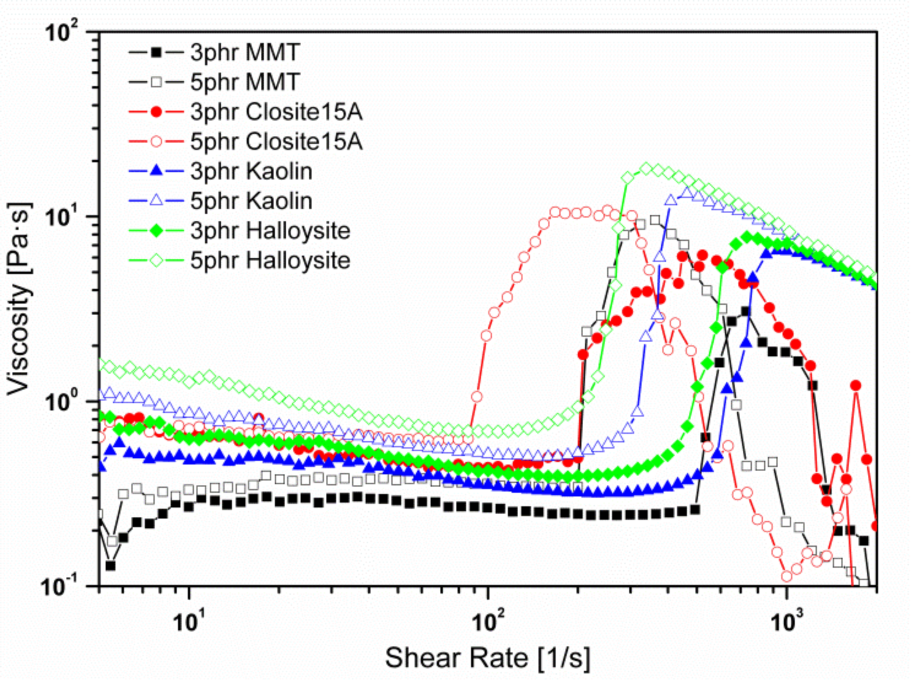


Figure 5.3 Steady-state viscosity profiles of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 25 ^{0} C



(a)



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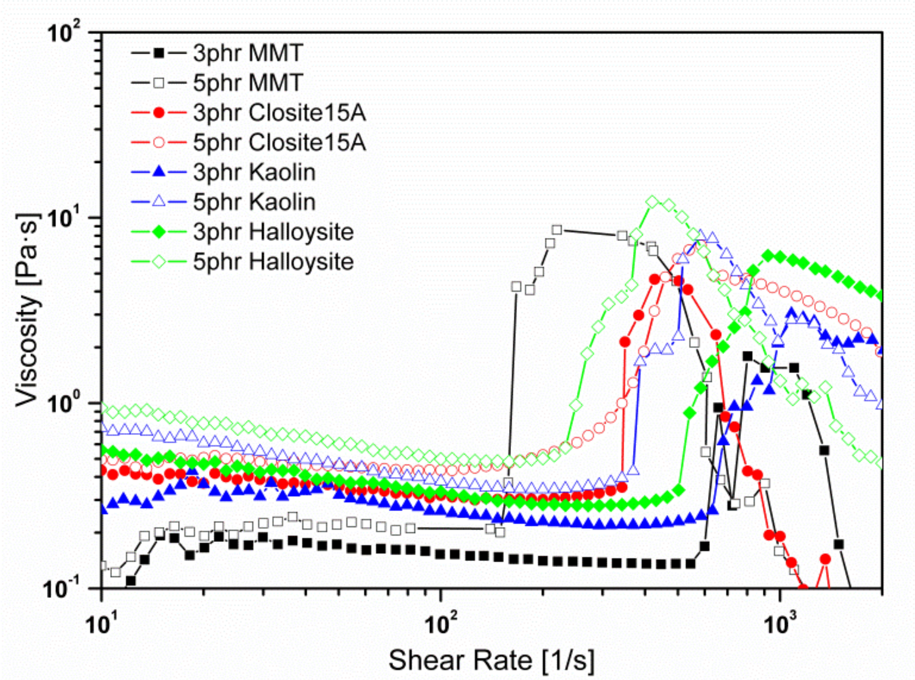
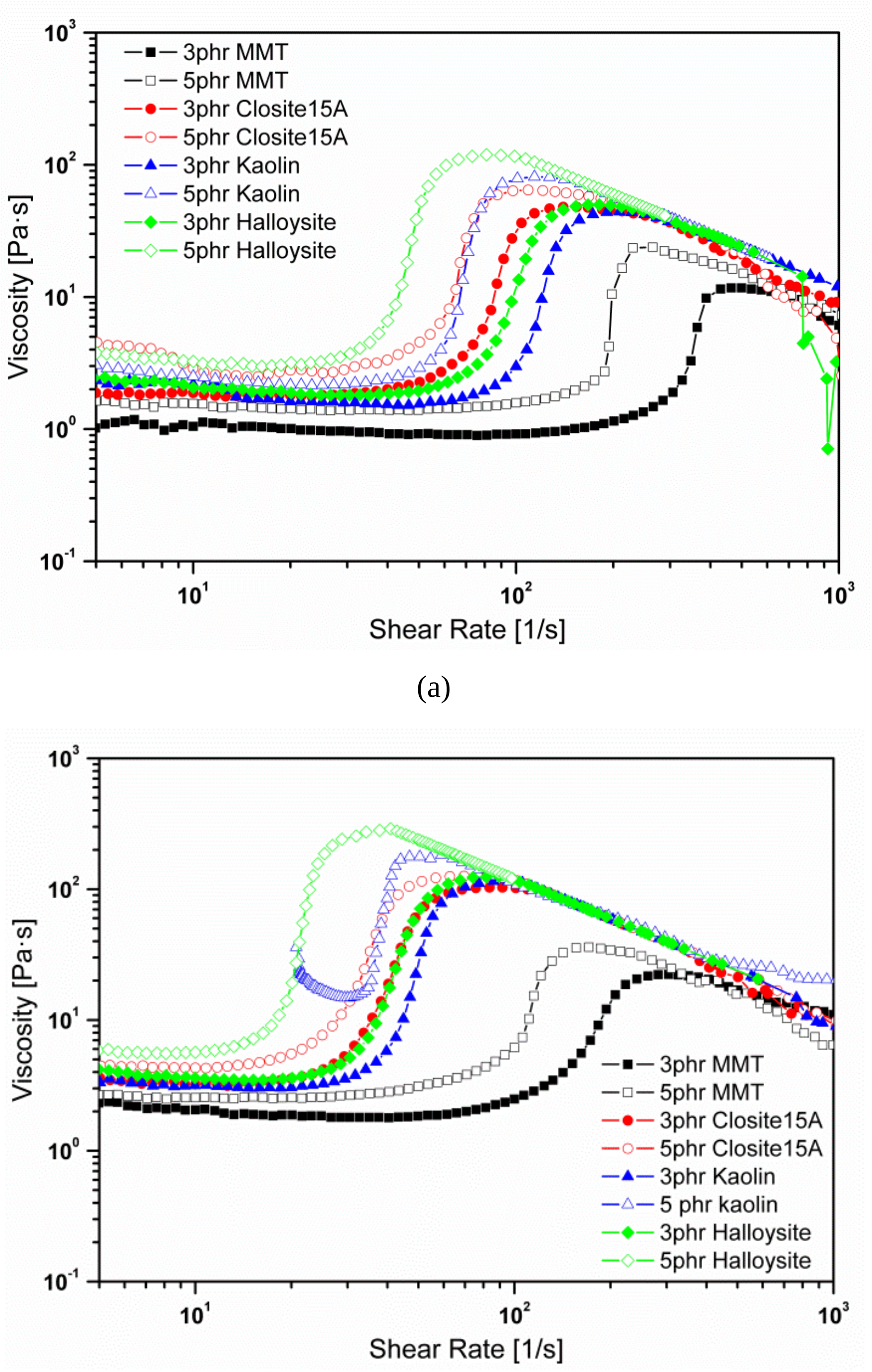


(c)

Figure 5.4 Steady-state viscosity profiles of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at a) 35 ^{0} C, b) 45^{0} C and c) 55^{0} C



(a)

(b)

Figure 5.5 Steady-state viscosity profiles of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at a) 15^{0}C b) 5^{0}C

In the next step of the steady-state rheological studies, the application point of view was focussed by studying the effect of temperature and the STF quality after a few days of storage.
To investigate the effect of temperature on the rheology of these systems, steady-state experiments were performed at 5^0, 15^0, 35^0, 45^0 and 55^0C. Figure 5.4a depicts that at a temperature of 35 ^{0}C all samples show a large decrease in critical viscosity values. Table 5.1 presents the comparisons of quantitative data for all samples at different temperatures. It can be noted that the same trend as for 35^0C is observed for 45^0C as given in table 3 and Figure 3b.

It has been noted that there is an appreciable decrease in viscosity for swelling clays i.e. STF containing MMT as well as Closite®15A additives. Also, Halloysite shows highest critical viscosity at both the temperatures for both the concentrations followed by Closite®15A.

At 55 ^{0}C, critical viscosity values are comparatively low (Figure 5.4c) and STF containing MMT and Kaolin as additives show a large decrease. As compared to all other clays 3 and 5 phr Halloysite again show the highest value of critical viscosity. As shown by Hasen *et.al* 2012, the increase in temperature leads to a transition from passive (non-swelling) to active (swelling clay) which leads to the expansion of the average interlayer distance [18]. This may be the reason for low shear thickening properties of STF containing Closite®15A. In general interaction between particles decrease as temperature increases which causes an increase in repulsive forces or degree of electrostatic repulsion [15, 19-21]. As temperature increase, the repulsive Brownian force intensifies the movement of particles thus making the cluster formation more difficult. Therefore, as borne out of rheological profiles, a high critical shear rate is required for formation of hydroclusters at high temperature. Temperatures above 55^0C have not been investigated as the viscosity of the base polymeric fluid (PEG200) will fall drastically i.e from 0.05 Pa.s at 20^0C to 0.012 Pa.s at 50^0C.

Additionally, the very low viscosity of the STF samples will increase the chance of the sample ejected out from the plate of rheometer giving inaccurate rheological profiles. At lower temperatures (5^0 and 15^0C) very interesting and potentially useful results are obtained. From Figure 5.5, it can be seen that again Halloysite as an additive shows the highest value of critical viscosity followed by Kaolin. Thus, it can be concluded that these non-swelling clays show a large change in critical viscosity at 5 ^{0} C compared to that at 25^0 C.

Table 5.1 Steady-state rheological parameters of STF with clay as additives at different temperatures

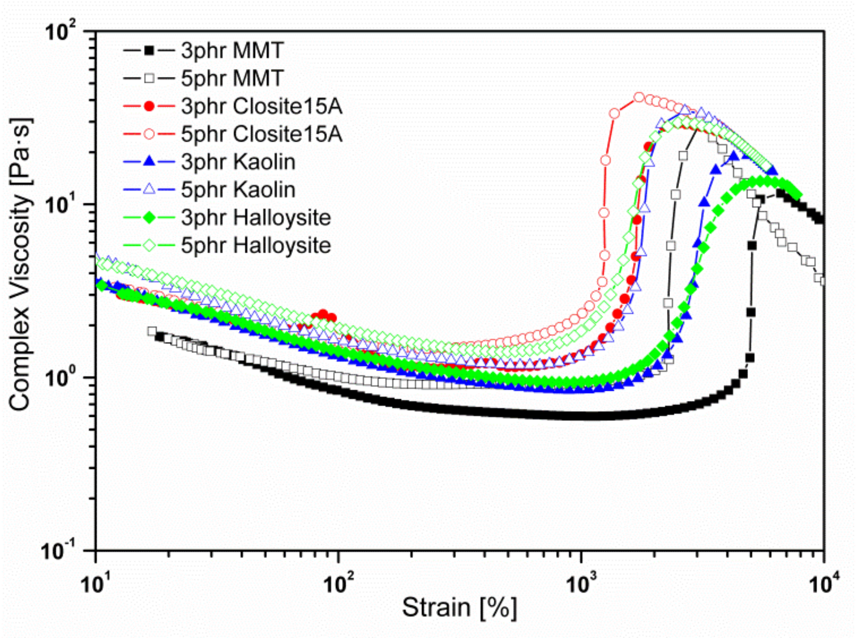
S.No	**Additives**	**Composition in 20 % fumed silica –PEG STF**	**Critical shear rate (s^{-1}) at different temperatures (^{0}C)**						**Critical viscosity (Pas) at different temperatures (^{0}C)**					
			5	**15**	**25**	**35**	**45**	**55**	**5**	**15**	**25**	**35**	**45**	**55**
1	MMT	3 phr	180	300	430	720	500	600	20	11	12	5	3	2
2		5 phr	100	200	200	250	210	150	35	25	27	8	9	8.5
3	Closite®15 A	3 phr	30	70	100	290	200	350	100	58	40	17	6	4.5
4		5 phr	20	15	70	120	100	220	125	65	55	28	11	7
5	Kaolin	3 phr	35	100	180	390	600	600	120	44	25	10	6.5	3
6		5 phr	20	50	80	200	300	320	170	82	47	24	13	8
7	Halloysite	3 phr	30	80	120	320	420	300	125	50	27	12	7	6
8		5 phr	15	25	52	100	210	200	275	115	50	36	18	12.5

However, swelling clays, MMT and Closite®15A do not show a significant corresponding change in viscosity at low temperatures. Similar behavior is obtained at 15^{0}C (Figure 5.5b). This indicates that temperature is an important factor for the performance of STF and therefore, should be taken in to account if STF impregnating soft body armor are to be made.

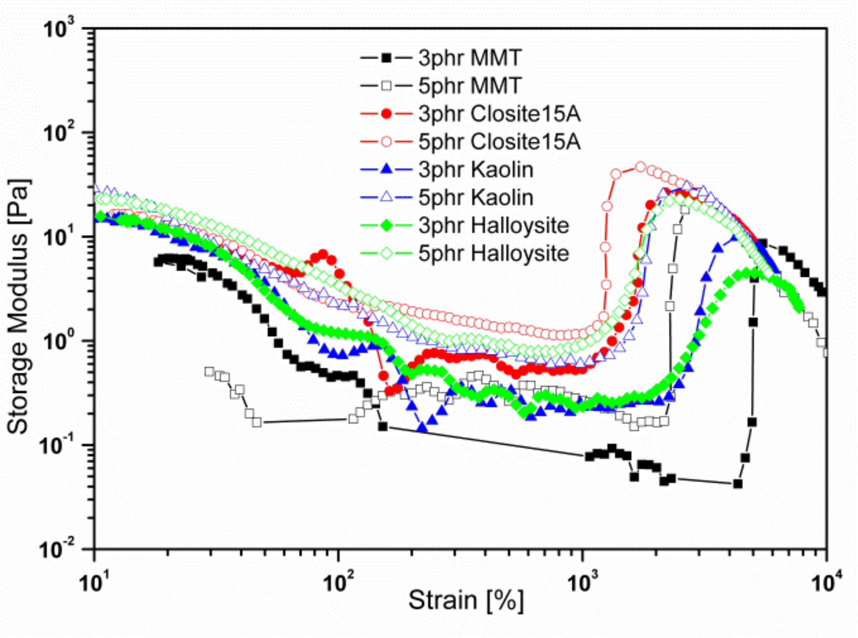
5.3.2.2 Dynamic-state rheology

Amplitude sweep

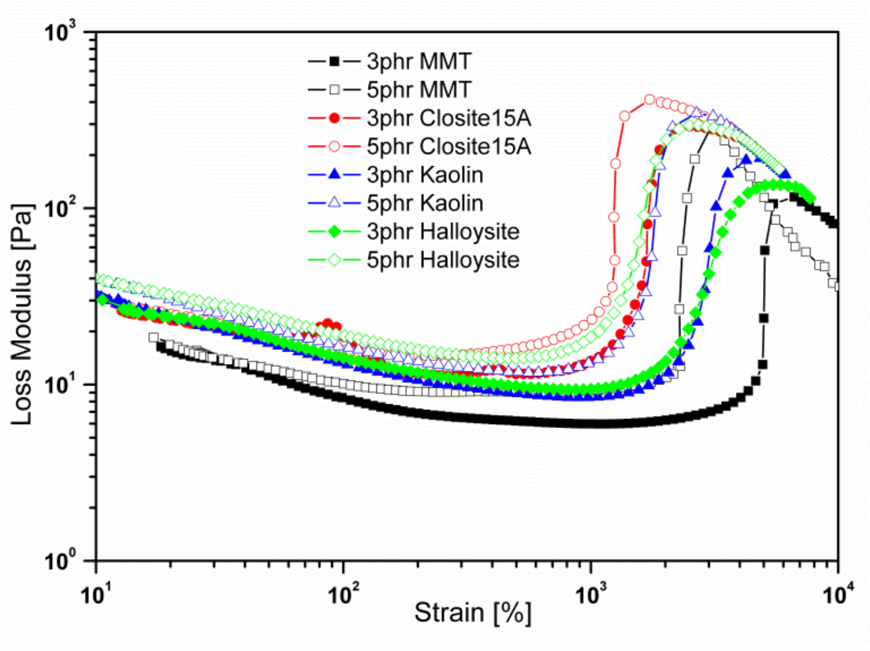
The damping capacity of STF was studied by strain sweeps versus G" and G' as well as η_c^* at constant frequencies of 10, 30, 50 and 70 rad/s. STF can show in general an increase in η_c^* and moduli after critical strain, and the increase depends on the concentration and the kind of particle used. The behavior at 10 and 30 rad/s are found to be same (Figures 5.6 and 5.7). Also, the profiles at 50 and 70 rad/s (Figures 5.8 and 5.9) are similar and vary only quantitatively compared to profiles at 10 and 30 rad/s. The profiles of loss modulus are qualitatively exactly same as that of complex viscosity profiles. Results of all profiles are tabulated in Table 5.2. Initially, at low strains, there is a movement of one layer of fluid past another with no transfer of matter resulting in linear viscoelastic properties. Thus, LVR (Linear Viscoelastic Range) implies a particular domain of strain up to which the microstructure of the STF system remains stable. Therefore, initially, similar to linear rheology is obtained as the network is not effectively established. But, beyond the critical strain, particles jump from one layer to another, dissipating a large amount of energy resulting in a sudden increase in complex viscosity. Similar observations were reported by Bird et.al 1987 [22]. The low strain profiles are specific to base (particle/polymer) system only as profiles at initial strains are almost constant regardless of the type of clay as an additive. Although, fragile conventional STF is dramatically changed to more viscous and elastic STF at high strains by simply adding nanoclays as the crosslinker for silica and PEG. It is believed that alignment along with the interaction of particles in the dynamic strain results in the formation of particle clusters resulting from bridging by clay particles.


3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite
Complex Viscosity [Pa·s]
Strain [%]
10^2
10^1
10^0
10^{-1}
10^1
10^2
10^3
10^4

(a)


3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite
Storage Modulus [Pa]
Strain [%]
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
10^3
10^4

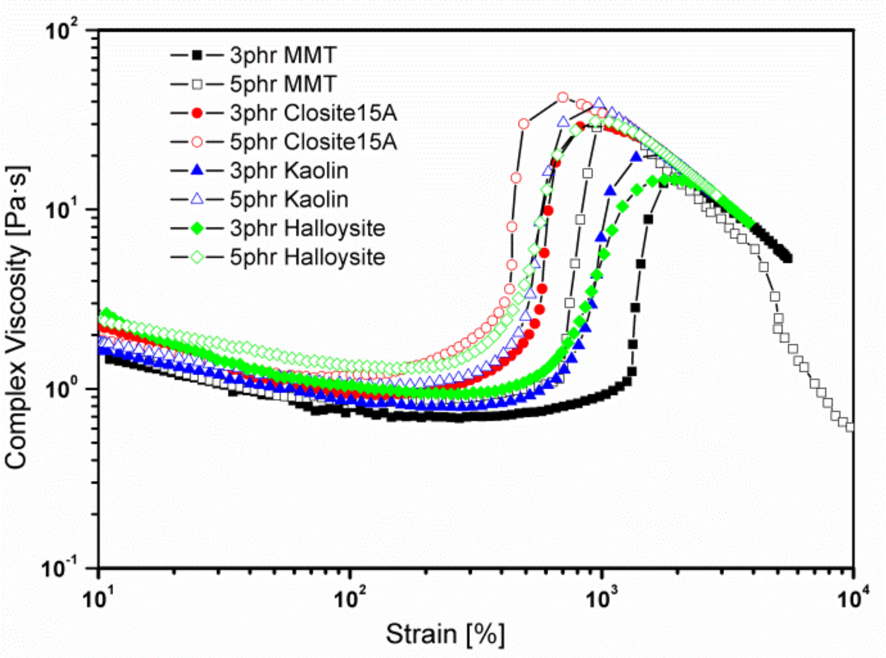
(b)



(c)

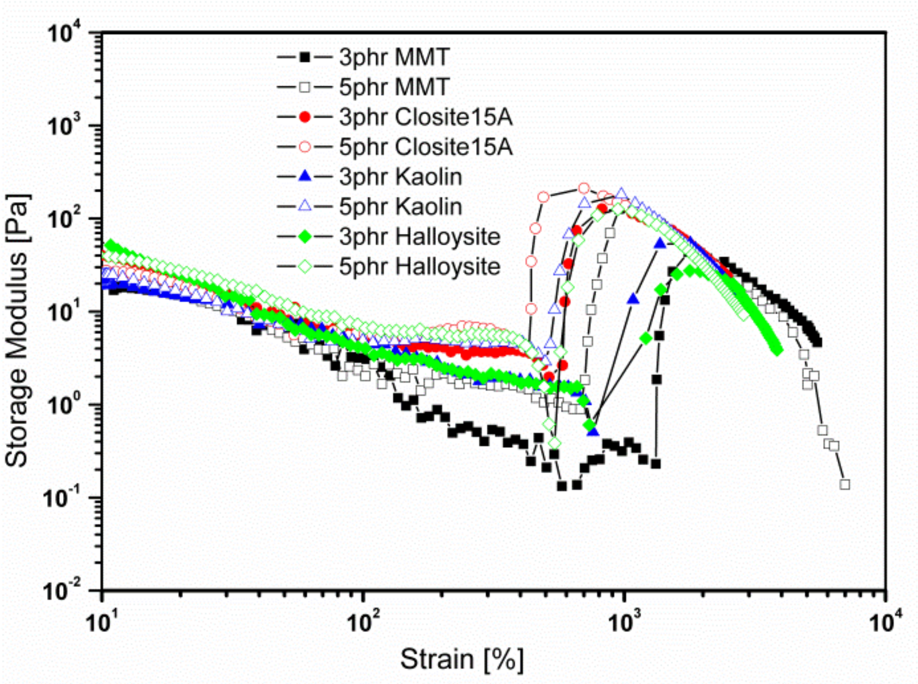
Figure 5.6 Strain sweep profiles of a) complex viscosity b) storage modulus and b) Loss modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 10 rad/s

Strain hardening is observed after the critical strain of 1000% as shown in Figure 5.6 at a constant frequency of 10 rad/s. 5 phr Closite®15A as a filler show maximum value of all the dynamic parameters (G', G" and complex viscosity). The increase in complex viscosity is explained by the phenomena of flow blocking by the formation of hydroclusters. This appears well with the literature on STF [23, 24]. Complex viscosity (Figure 5.6a) for Closite®15A and Halloysite as fillers (about 55 Pa.s and 45 Pa.s respectively) is consistent with steady-state viscosities (Figure 5.2). However, all other STF show a slight decrease in complex viscosity compared to their respective steady-state viscosity. At a low frequency of 10 rad/s, STF experience high critical strain values as depicted in Table 5.2. The behavior of 3 phr Closite®15A is similar to 5 phr Halloysite and Kaolin. i.e under oscillatory flow field the shape of particles does not have observable differences. Further, profiles of moduli show that there is no gelation as G" is always greater than G' [25].



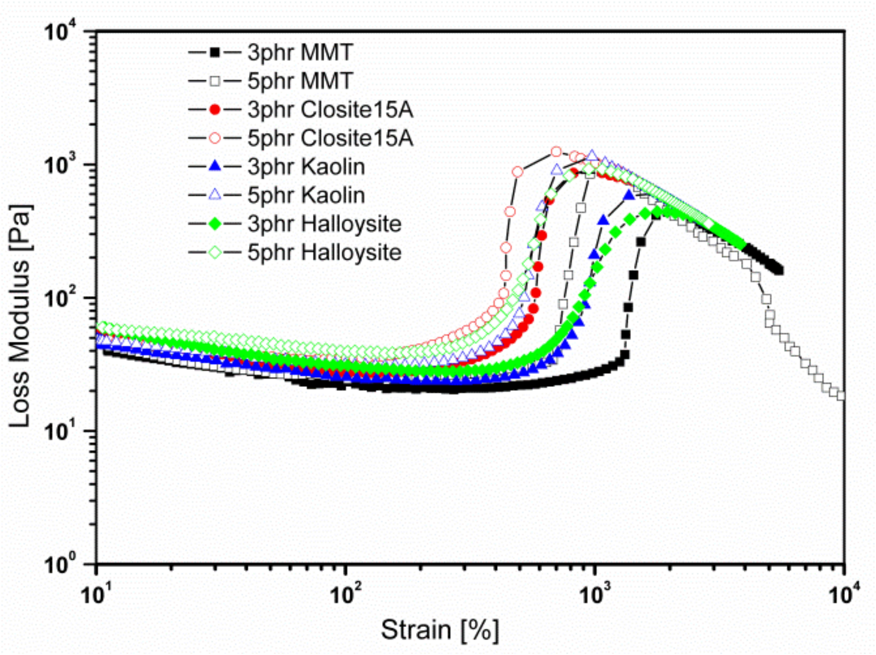
Complex Viscosity [Pa·s]
Strain [%]
10^{2}
10^{1}
10^{0}
10^{-1}
10^{1}
10^{2}
10^{3}
10^{4}
3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite

(a)



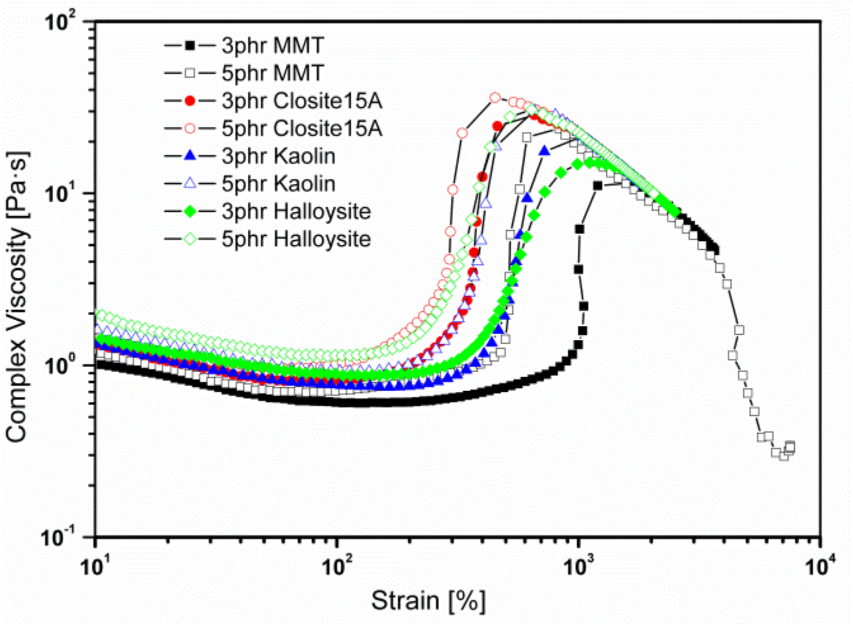
Storage Modulus [Pa]
Strain [%]
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{1}
10^{2}
10^{3}
10^{4}
3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite

(b)

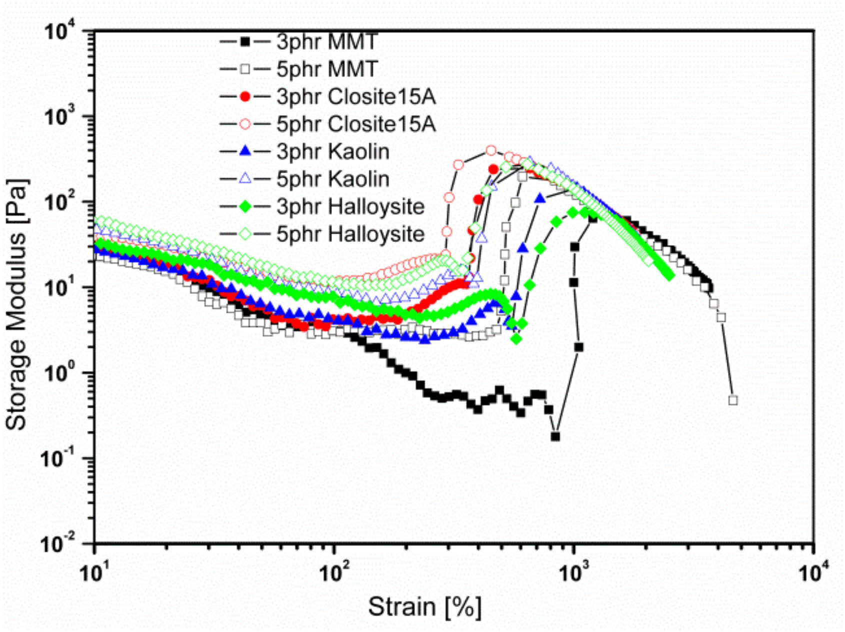


(c)

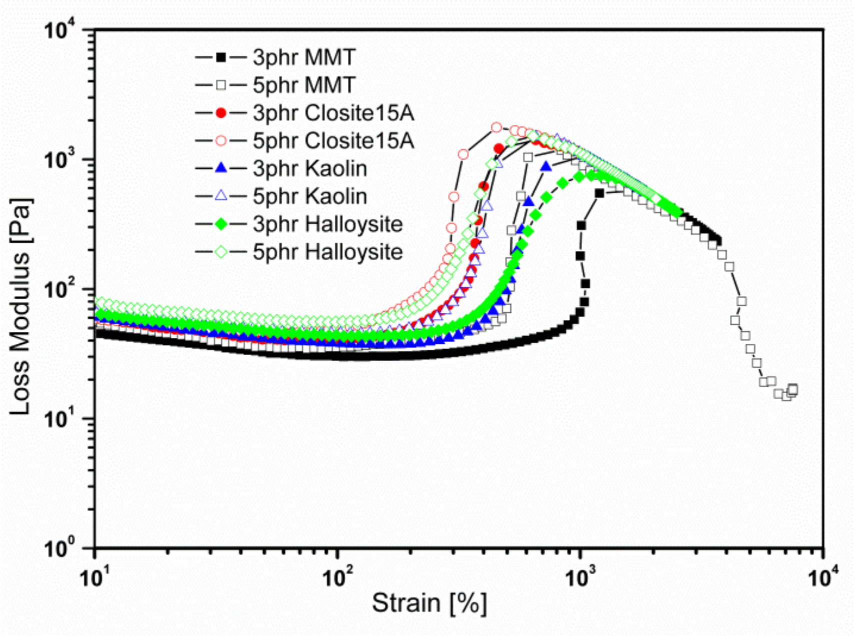
Figure 5.7 Strain sweep profiles of a) complex viscosity b) storage modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 30 rad/s



(a)

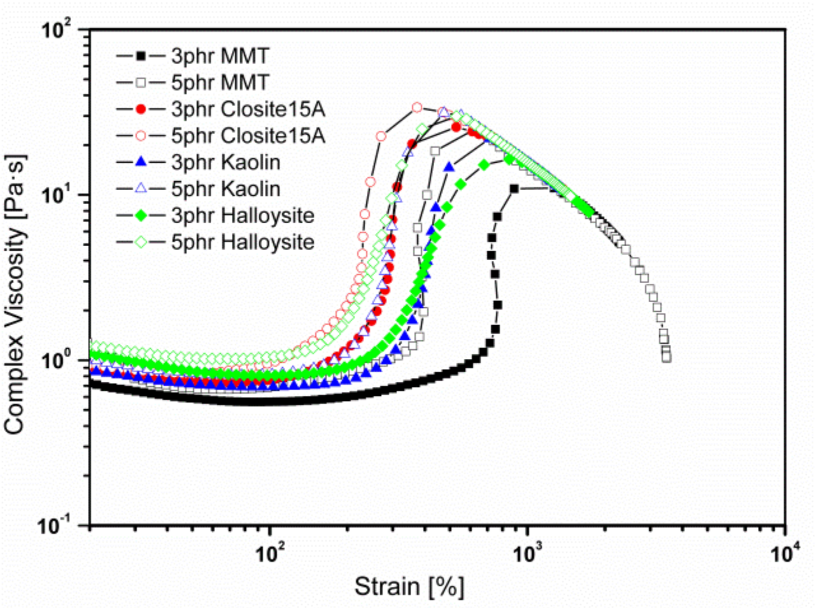


(b)

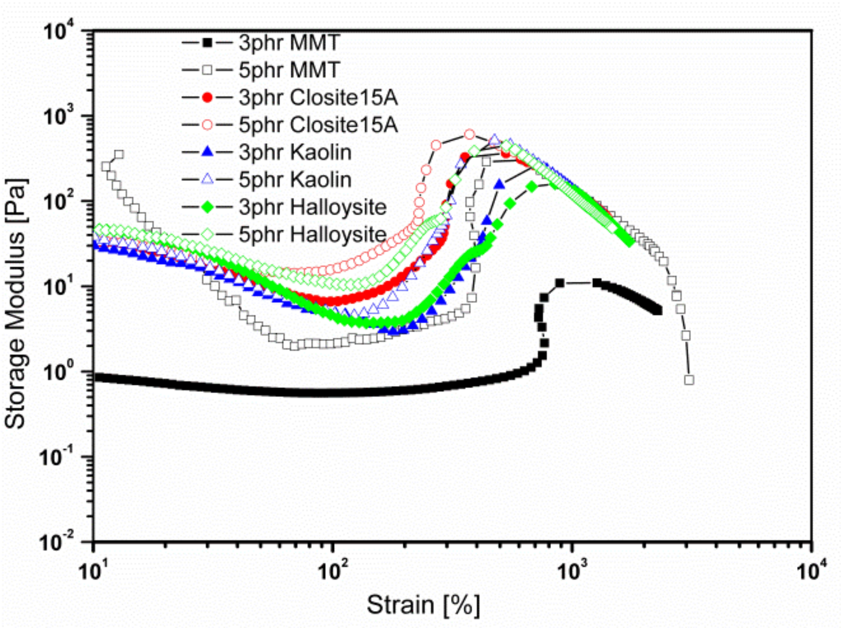


(c)

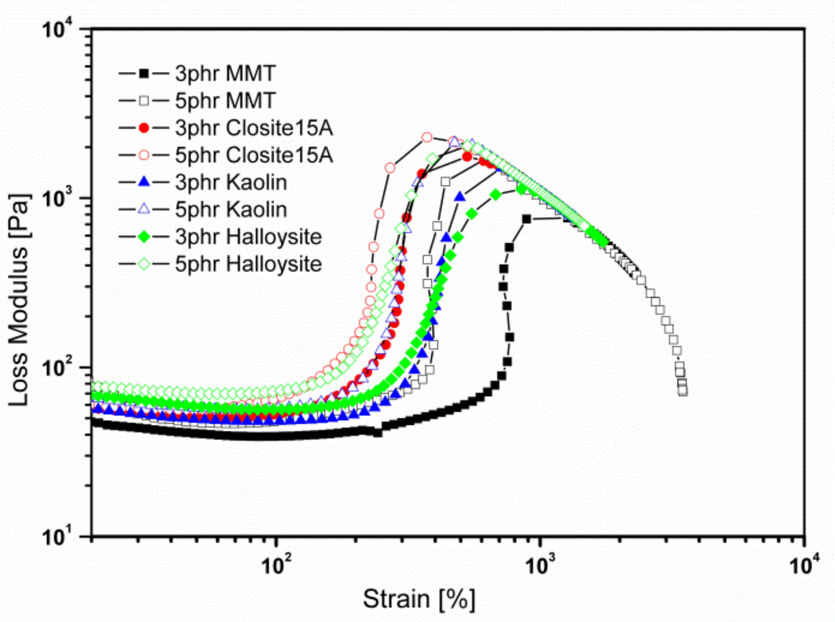
Figure 5.8 Strain sweep profiles of a) complex viscosity b) storage modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 50 rad/s


3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite
Complex Viscosity [Pa·s]
Strain [%]
10^2
10^1
10^0
10^{-1}
10^2
10^3
10^4

(a)


3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite
Storage Modulus [Pa]
Strain [%]
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
10^3
10^4

(b)



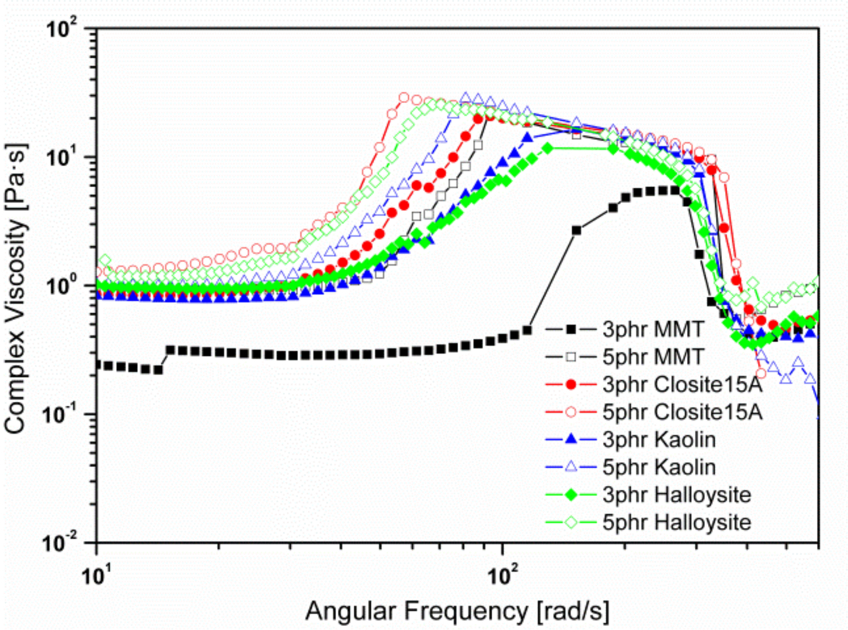
(c)

Figure 5.9 Strain sweep profiles of a) complex viscosity b) storage modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 70 rad/s

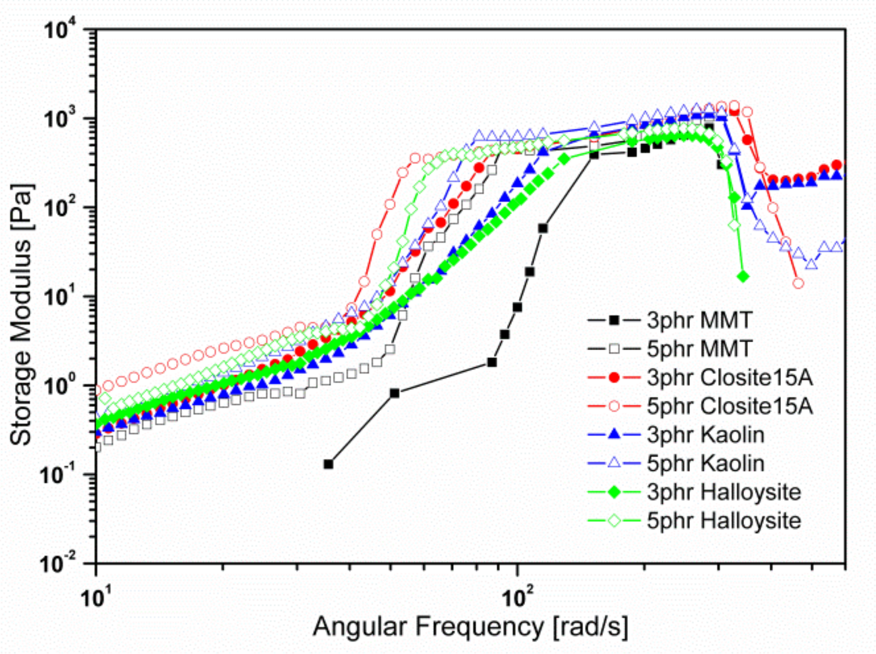
For 70 rad/s (Figure 5.9) except the complex viscosity, all the dynamic parameters change significantly as compared with those obtained at strain sweep at 10 rad/s. Strain hardening is observed after 100% strain. This shows that at high-frequency, STF does not get enough time for relaxation and this leads to an increase in complex viscosity starting at the low critical strain. Thus, from Table 5.2 it can be concluded that the high shear force applied to the STF at high frequency increases the shear thickening more, evidently resulting in cross-linking hydroclusters at a fast rate than in a low-frequency rheological profiles.

Table 5.2 Strain sweep at different frequencies.

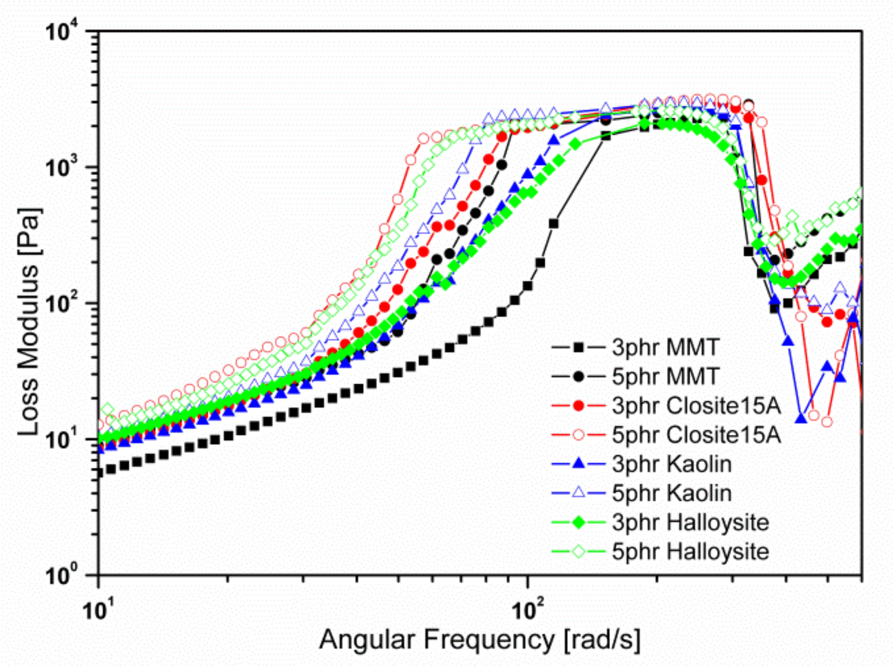
Frequency (rad/s)	Strain thickening range (%)	Critical complex viscosity η_c (Pa.s)	Storage Modulus G' (Pa)	Loss Modulus G'' (Pa)
10	600-3000	45	50	400
30	200-1000	44	250	1200
50	120-800	40	500	1800
70	105-450	35	800	2700


Complex Viscosity [Pa·s]
Angular Frequency [rad/s]
10^2
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite

(a)


Storage Modulus [Pa]
Angular Frequency [rad/s]
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
3phr MMT
5phr MMT
3phr Closite15A
5phr Closite15A
3phr Kaolin
5phr Kaolin
3phr Halloysite
5phr Halloysite

(b)

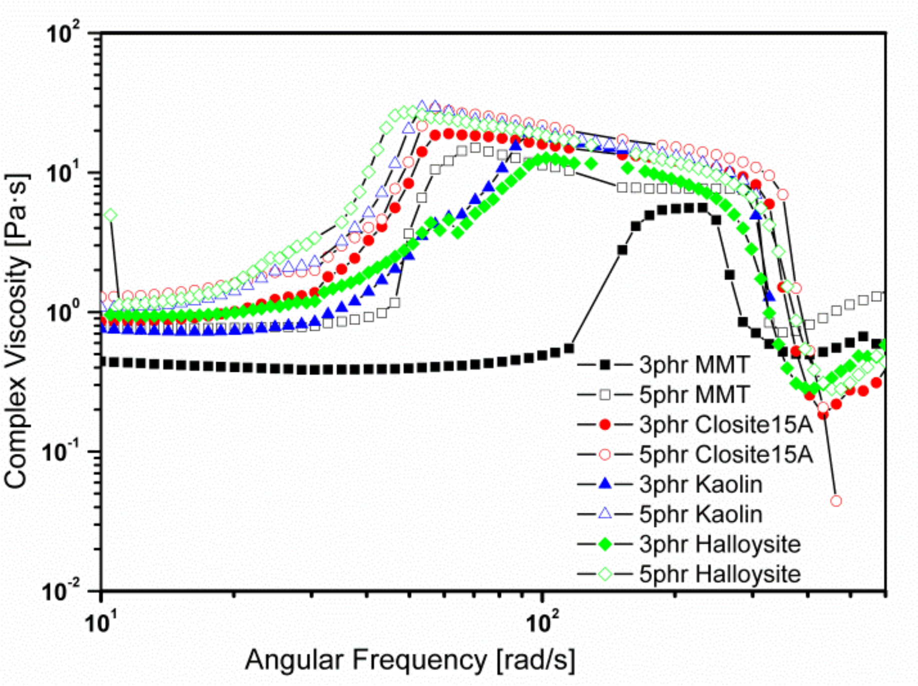


(c)

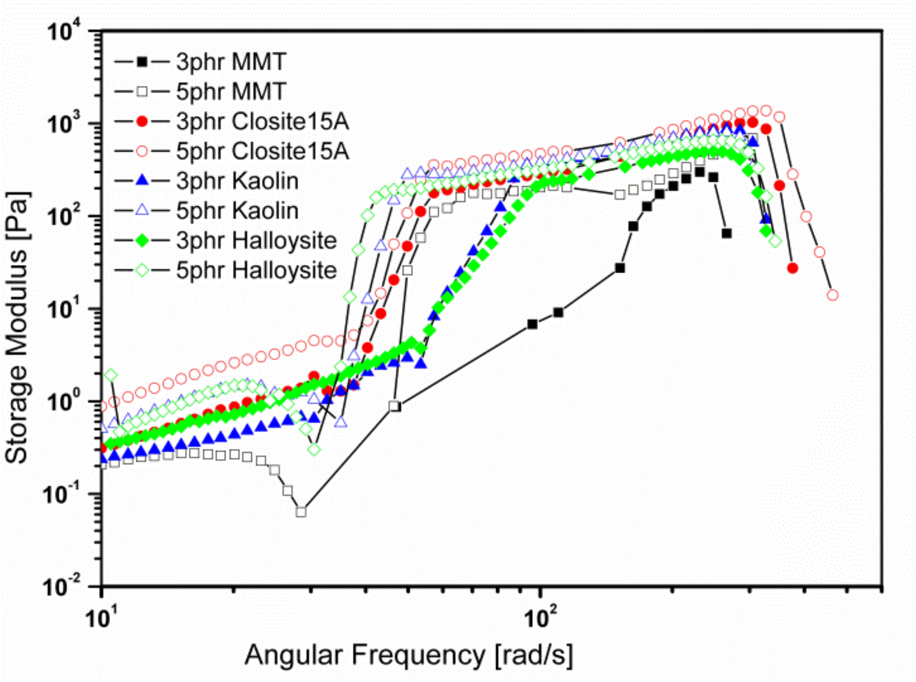
Figure 5.10 Frequency sweep of a) complex viscosity and b) storage modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 500% strain

Frequency sweep

All samples were investigated by frequency sweeps at different constant strains. As from Table 5.2, it can be concluded that all samples show the shear thickening in the range of strains from 450% to 3000%, at all four frequencies considered therefore frequency sweeps were studied at constant strains of 500, 700, and 900 %. Frequency sweep at a constant strain of 500% is shown in Figure 5.10. Profiles at 700 and at 900 % (Figures 5.11 and 5.12) do not show much difference when compared with profiles at 500% strain as tabulated in Table 5.3. A slight decreasing plateau region is observed for complex viscosities after a critical frequency, whereas for both the moduli the plateau region is slightly increased after the same critical frequency value. When storage modulus becomes independent of frequency it is indicative of solid nature. The descending order of the η_c^* is Closite®15A, Halloysite and Kaolin followed by MMT. Even, 3 phr Closite®15A shows higher values than 5 phr MMT. The plateau region for 900% strain shifts to lower frequency values as compared to frequency sweep at 500% strain. This is preciously what is observed from the range of non-linear behavior as seen in Table 5.2. A large decrease in values is noted for 3 phr MMT at low frequencies.



(a)



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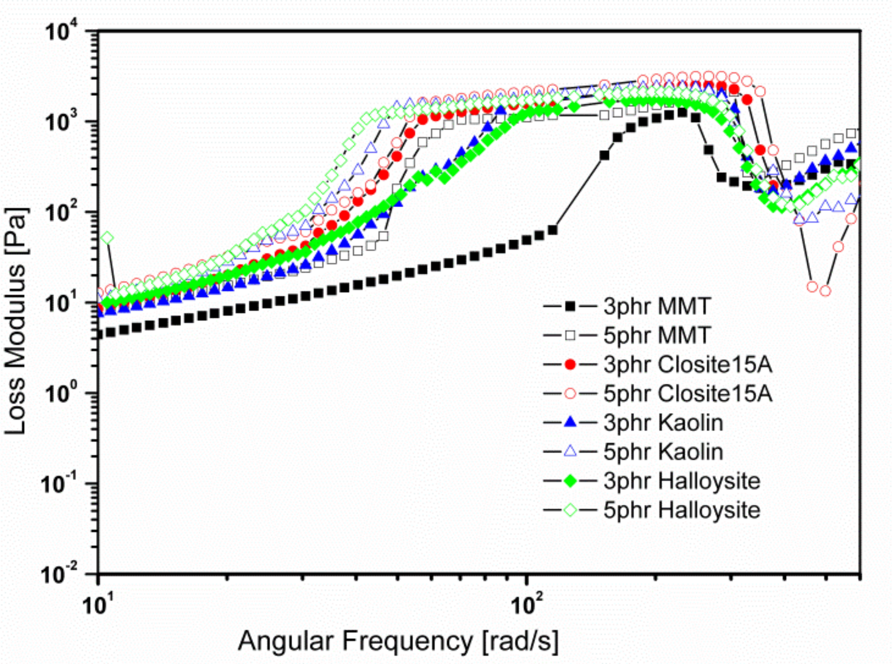
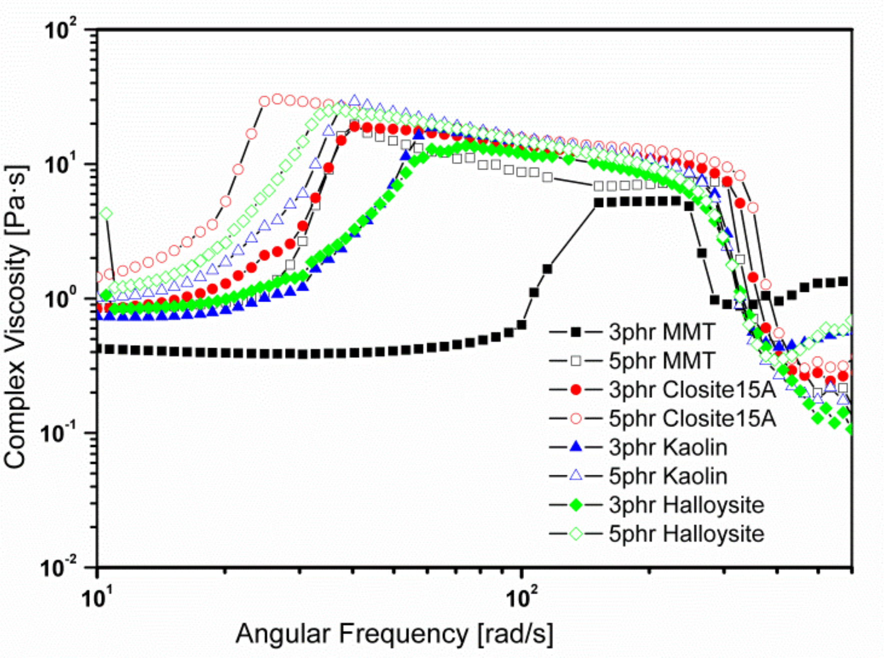
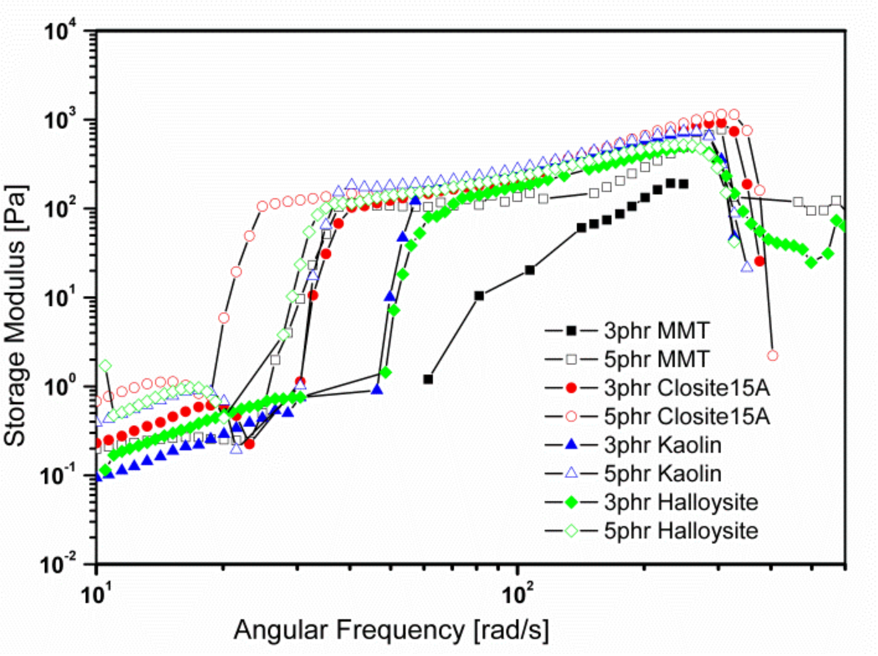


(c)

Figure 5.11 Frequency sweep of a) complex viscosity and b) storage modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 700% strain



(a)



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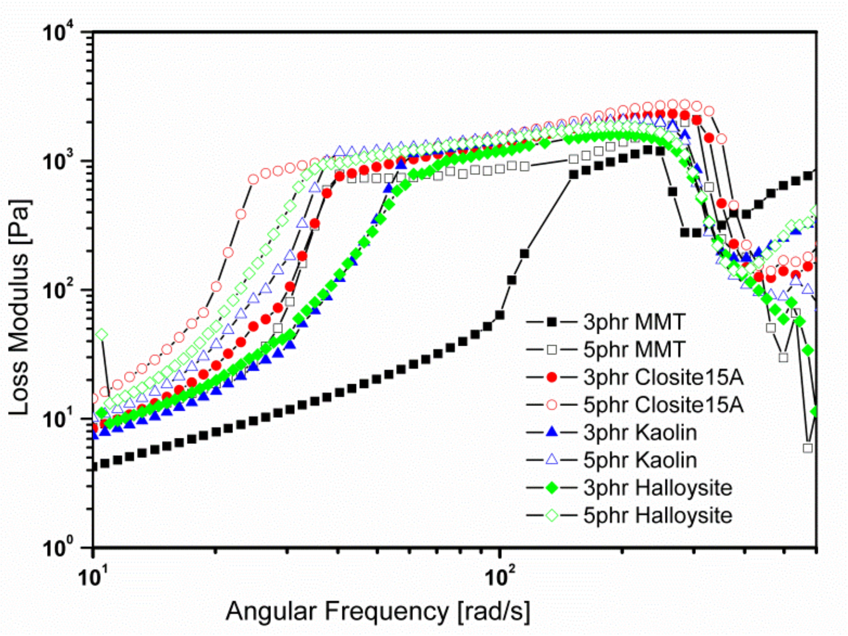

(c)

Figure 5.12 Frequency sweep of a) complex viscosity and b) storage modulus of 20% fumed silica-PEG STF containing different nanoclays at different concentrations at 900% strain

Table 5.3 Frequency sweep at different strain%

Strain (%)	Range of non-linear behavior (rad/s)	Critical complex viscosity η_c^* (Pa.s)	Storage Modulus G' (Pa)	Loss Modulus G" (Pa)
500	30-310	30	1170	3010
700	25-300	35	1190	4000
900	10-290	33	1180	3000

5.3.3 Stability

The sensitivity of the shear viscosity to shear history and sample age was most apparent in the concentrated samples due to possible aggregation of particles with time. For MMT clay at a concentration of 3 phr, after a month deposition or settling of clay at the bottom could be seen, however, for all other samples, no phase separation was observed. Rheological studies after 40 days showed that STF were still visually homogeneous and exhibited shear thickening properties, with only a slight (10-20%) decrease in overall viscosity values as observed in Figure 5.13. High concentration samples lead to more decrease in shear thickening properties.

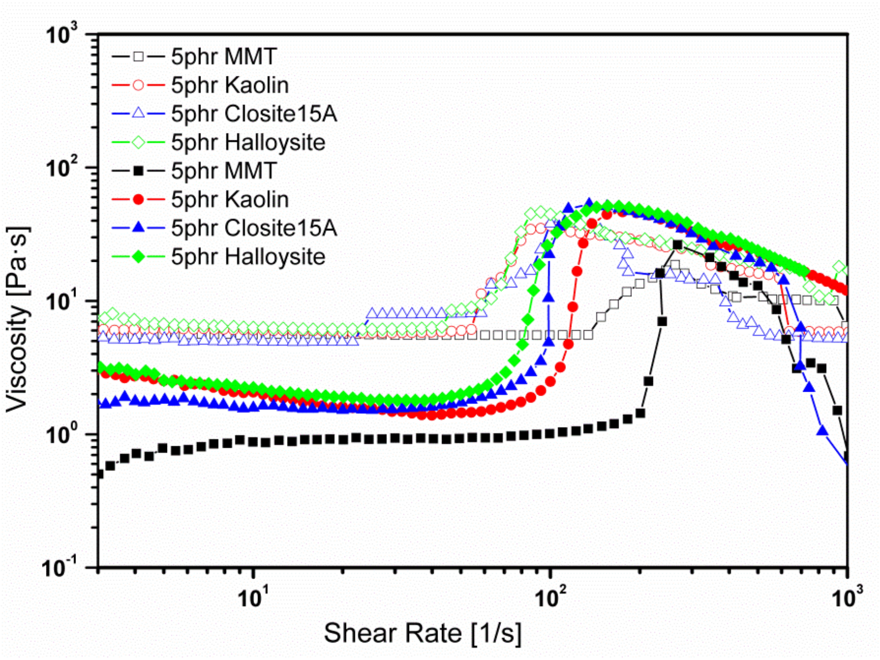

Figure 5.13 Steady-state viscosity profiles of 20% fumed silica-PEG STF containing 5phr of different nanoclays after a storage time of 0 days (close symbol) and 40 days (open symbol)

Figure 5.13 shows the effect of storage time on the rheology of STF. The rheology profiles showed that with an increase in storage time, the shear thickening behavior decreases. The observed changes in shear thickening behavior can be explained by the flocculation of some particles with time. Although the critical viscosity values of fresh STF samples are much higher than those stored for 40 days, it is noted that STF still exhibit shear thickening even after weeks. However, zero shear viscosity does not change too much for all samples. This significant decrease with storage indicates the gel formation.

Table 5.4 A comparison of results from the present study with those reported in literature (3, 27-29)

Dispersed particles	Total weight percentage in PEG200	Critical viscosity **(Pas)**	Critical shear rate **(s^{-1})**
Results reported in literature			
Silica 100 nm	50	40	5
	20	24	400
Fumed silica 14 nm	30	35	250
	40	36	230
Results from present study			
Fumed silica11 nm and Closite®15A	23.81	55	70
Fumed silica11 nm and Halloysite	23.81	50	52
Fumed silica11 nm and Kaolin	23.81	47	80

In Table 5.4 presents a comparison of present study with those reported in literature. It can be seen that 5 phr concentration of different clay as additives in STF have increase critical viscosity values at much lower overall particle concentration.

5.4 Conclusion

The study shows that silica-polymer STF with clay as additives, exhibit extraordinary properties. The processing of STF was achieved, not by the mere incorporation of clay nano-particles into a silica-particle network, but by allowing the clay platelets to act as a substrate for silica particles in the formation of polymer/silica networks i.e hydroclusters. From steady-state profiles, it is confirmed that non-swelling clays show an increase in properties at both high and low temperatures. Thus, temperature studies imply that these STF could bear a large range of temperatures in their practical applications. Additionally, results verify that the STF have a stable shear thickening effect up to four weeks after which it required re-sonication to be used for practical applications. Strain sweep shows that profiles of all clays as additives are similar at different frequencies whereas quantitatively they are significantly different.

Closite®15A as an additive gives high values of all the dynamic parameters, which confirms the highly viscoelastic nature of this STF as compared to all others, as it forms high strength network. A large increase in storage modulus (elasticity) as frequency increases from 10 to 70 rad/s confirms a high degree of the cross-linked structure resulting in high impact resistance properties. In frequency sweep profiles for different clays is qualitatively similar and quantitatively slightly decreases as constant strain value increases from the constant strain of 500 to 900%. The critical strain at which the shear thickening is obtained for the samples studied varies from 500 to 3000% and critical frequency varies from 10 to 300 rad/s. The physical interpretation for these values is that the very thin layer of STF would extend 10 to 30 times, on impact, after which the STF layer would become semi-solid.

Thus it was shown that the properties of clay particles used as an additive and concentration significantly affect the rheological properties of STF (as shown in Table5.4). Additionally, the temperature has a marked effect on STF performance. When nanoclays are added to the reference/base STF of 20% fumed silica-PEG200, effects are produced which depends on the morphology and properties of clays. The particle motion in the STF is restricted at much lower particle loading when high aspect ratio clay particles were added. Also, clay particles increase interaction between particles and with the carrier fluid resulting in the enhanced dispersion which increases the stability of STF over a long time of storage and increases the range of shear thickening behavior. Thus, the study considers the importance of clay as an additive and its morphology, modification, and rheology on fumed silica-PEG STF and describes how these properties can be leveraged to induce high shear thickening behavior to be utilized for high impact applications.

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Chapter 6 Effect of addition of nanomer to 20% fumed-silica-PEG STF

In Chapter 5, it was seen that modified MMT Closite®15A shows a better performance under both steady-state and dynamic oscillatory rheology, therefore rheology of another organically modified MMT clay, Nanomer I.28E as nano-filler has been studied under a wide range of shear rate, strain rate, temperature and frequency. Further a study was undertaken to investigate if there is any difference in rheology, if instead of nanoclay, an equal weight % of additional fumed silica is added to the reference STF of 20% fumed silica-PEG200.

This chapter is based on: Rheology of Fumed Silica and Polyethylene Glycol Shear Thickening Suspension with Nanoclay as an Additive; Mansi Singh , Sanjeev K Verma, Ipsita Biswas and Rajeev Mehta; Defence Science Journal; DOI: https://doi.org/10.14429/dsj.69.12420 (IF: 0.589)

6.1 Introduction

In the present study, the motivation was to study the rheology of suspensions containing fractal fumed silica particles and high aspect ratio nano-scale additive i.e to replace the expensive spherical silica particles by comparably less amount of fumed silica and nanoclay and also to achieve high critical viscosity as well as high critical shear rate which are the prerequisite for many applications including soft body armor. The 20% of fumed silica-PEG is taken as reference STF and the effect of different concentration of nanoclay and fumed silica has been studied and compared under both steady-state and dynamic-sate rheology.

6.2. Processing

A sonication time of 10 min by a probe sonicator at 40% amplitude was found to be optimum for the fumed silica-PEG system of 20ml volume (Figure 6.1a and b). For samples containing nanomer clay as nano-additive, the suspension of clay and PEG were first sonicated for 2 min prior to addition of fumed silica to break the structure comprising of stacked platelets, otherwise coagulation can take place (Figure 6.1c). The concentration of clay particles less than or equal to 5 phr facilitates proper exfoliation/intercalation of high aspect ratio clay particles [1]. Therefore, clay particles were added at a low concentration of 3, 4 and 5 phr (parts per hundred of resin) in 20 weight % STF of fumed silica and PEG (Figure 6.2).

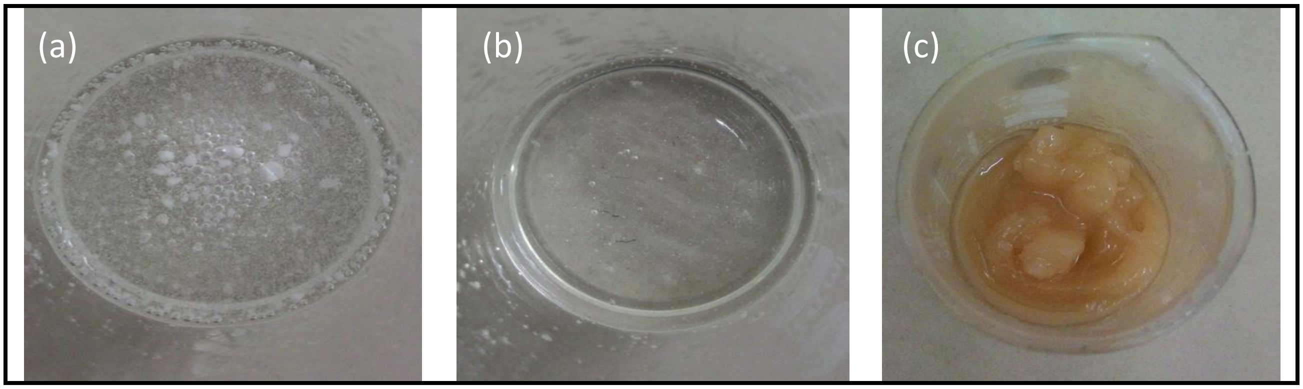


Figure 6.1 Fumed silica dispersed in PEG a) without sonication b) with sonication c) with clay as filler resulting in agglomerates due to improper mixing.

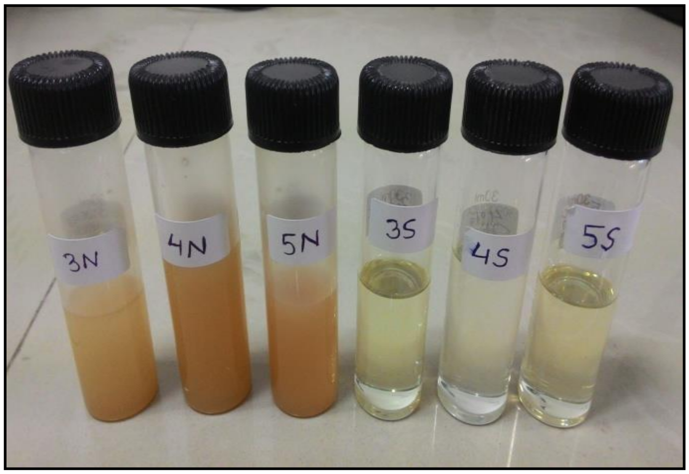


Figure 6.2 Glass vials containing STF samples where ‘N’ denotes Nanomer clay and ‘S' denotes fumed silica as additives with numbers representing concentration in phr

6.3 Results and discussion

The rheological analysis was done by using Rheometer (MCR52, ANTON PAAR) with cone and plate geometry with a plate diameter of 40mm and a cone angle of 1^0. All steady-state measurements were conducted at 25^0, 35^0, $45^0$and 55^0 C with temperature control provided by peltier elements of the rheometer.

6.3.1 Steady-state rheology

The viscosity profiles for 3, 4 and 5 phr of nanoclay as an additive to 20 weight % fumed silica-PEG STF are shown in Figure 6.3. All the results were obtained at 25^0C. It can be seen that there are three well-defined viscosity regions present. The first viscosity region is the shear-thinning region, which is due to an arrangement of particles in the direction of flow of the polymeric liquid (PEG) under low shear conditions, followed by a second region where the increase in viscosity values occurs due to the formation of hydroclusters. The third region once again corresponds to shear-thinning region due to rupture of hydroclusters under high shear rates, after which no shear-thickening was observed. Additionally, at higher shear rates, the liquid polymer contribution to viscosity dominates and the effect of the additive decreases as confirmed by the same decreasing value of viscosity for all samples. As no discontinuities were observed in the viscosity profiles in this region, hence, both the possibility of instabilities which can cause a portion of the samples to be ejected out from the rheometer plate at very high shear rates resulting in a decrease in torque with decrease in the viscosity or the occurrence of wall slip can be ruled out.

In the second viscosity region, as shear rate increases to critical shear rate, viscosity exhibits a sharp increase for mono-disperse STF of fumed silica particles as particles having similar characteristics form clusters easily. However, the increase is relatively smooth for bi-disperse STF of fumed silica and clay with the transition spreading over a wide range of shear rates. The possible reason for this is that the charge stabilized (fumed silica) dispersions exhibits a greater shear thickening microstructure distortion as compared to charge-neutralized (nanoclay) dispersions [2]. As polydispersity makes ordering difficult [3] therefore 20% silica monodisperse with, 3, 4 and 5 phr fumed silica particles shows more shear thickening than nanomer as filler in bidisperse shear thickening fluids. Although, STF with nanoclay, however, have higher critical shear rates when compared with pure fumed silica-PEG STF. Additionally, the phenomena of Ferris effect in rheology also describes that a broader particle size distribution (i.e, clay and nano-silica particles) yields a low viscosity than a narrow particle size distribution (only fumed silica particles), for the same concentration of particles [4, 5].

As the outer layers of clay platelets are permanently negatively charged, thus when different clay particles would try to fit in clusters at high shear rates they would face electrostatic repulsion thus, higher critical shear rate values are required to form clusters in nanoclay containing STF when compared with no-clay STF. This is contrary to results reported by Maranzano and Wagner [6] wherein they reported an increase in critical viscosity values as particle size increases however in the present study, nanoclay in the bi-disperse suspension is not only bigger in size than nano-fumed silica, it is also different with regard to shape. As in earlier attempts to make only nanoclay-PEG STF up to even 60% concentration did not succeed as shown in Chapter 4, thus, it can be concluded that in the present study of the bidisperse system, only fumed silica is responsible for the shear thickening behavior. However, the critical viscosity of pure 20% fumed silica STF (11 Pa.s) is less than the bidisperse system (20 Pa.s), that suggests that presence of clay has a positive effect on critical viscosity of STF, but this effect is less than that obtained from the same weight percentage of fumed silica particles (40 Pa.s).

Further, organically modified clay increases the interaction between the clay platelets and solvent by neutralizing the charges between the layers [7]. This results in a decrease of shear stress required to generate hydroclusters as the concentration of clay increases and therefore shear thickening occurs at low stresses. Additionally, ionic modification of clay helps to reduce the tendency of clay agglomeration during the dispersion in the suspension medium by reducing interlayer attractive forces and thus aids in intercalation or exfoliation of clay particles.

Results of the addition of nanoclay STF indicates that the network of particles formed at the onset of shear thickening is small when compared to monodisperse nano-silica STF but are more interconnected and stronger as suggested by large values of viscosities at very high shear rates. Intriguingly, the values of the critical shear rate are nearly independent of the type of particles used as an additive and depend only on add-on concentration of additive and critical shear rate decreases as concentration increases. However, with regard to critical viscosity, the samples with 3 and 5 phr clay showed marked shear thickening and high post-transition viscosity. The increase in viscosity varies with a wide range i.e. from a minimum about 20 Pa.s (for 3 phr nanoclay) to a maximum of about 74 Pa.s (for 5 phr nano-silica) when compared with reference STF (about 11 Pa.s). For all STF studied, the critical shear rate was found to be inversely proportional to the critical viscosity of the suspension and the results have been tabulated in Table 6.1.

Table 6.1 Steady-state rheological parameters

Sample code	Additive	Add-on weight (phr)	Critical viscosity (Pa.s)	Critical shear rate (1/s)
3N	Nanomer	3	20	115
3S	Fumed silica	3	40	113
4N	Nanomer	4	33	93
4S	Fumed silica	4	60	87
5N	Nanomer	5	55	54
5S	Fumed silica	5	74	62

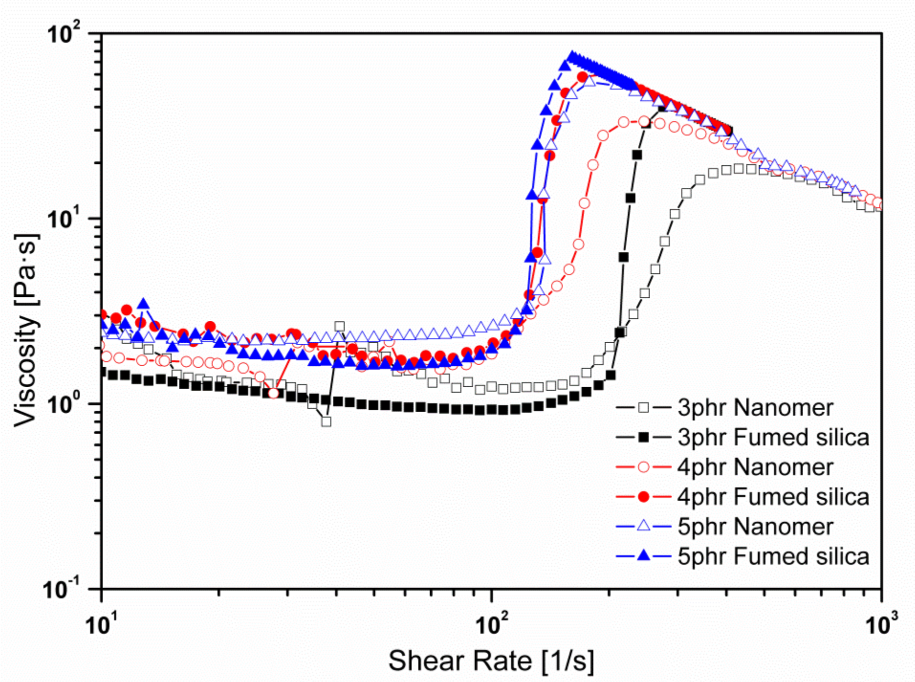
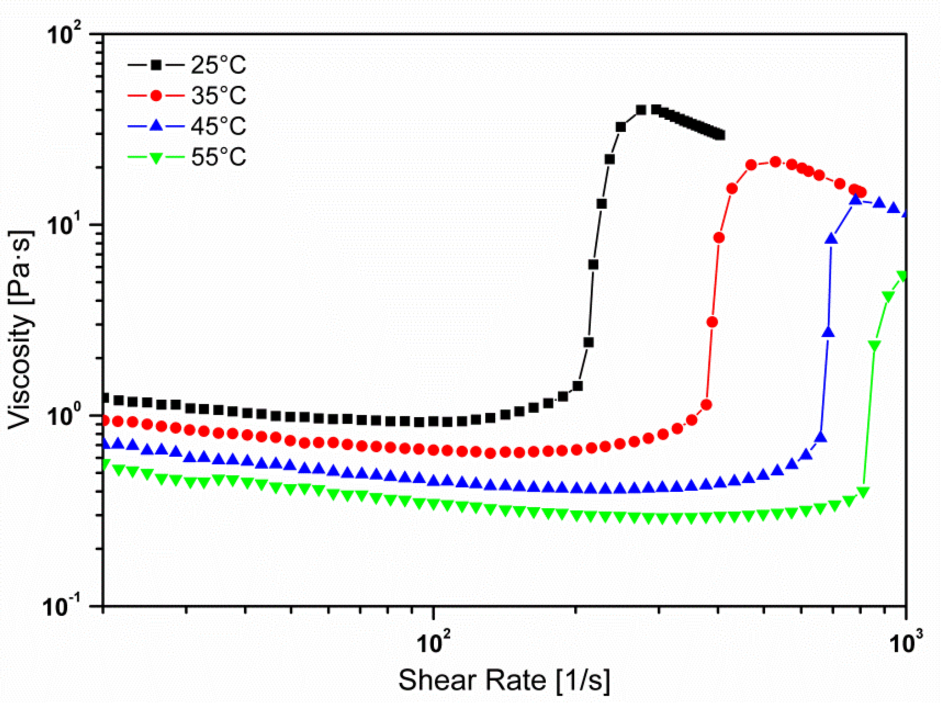
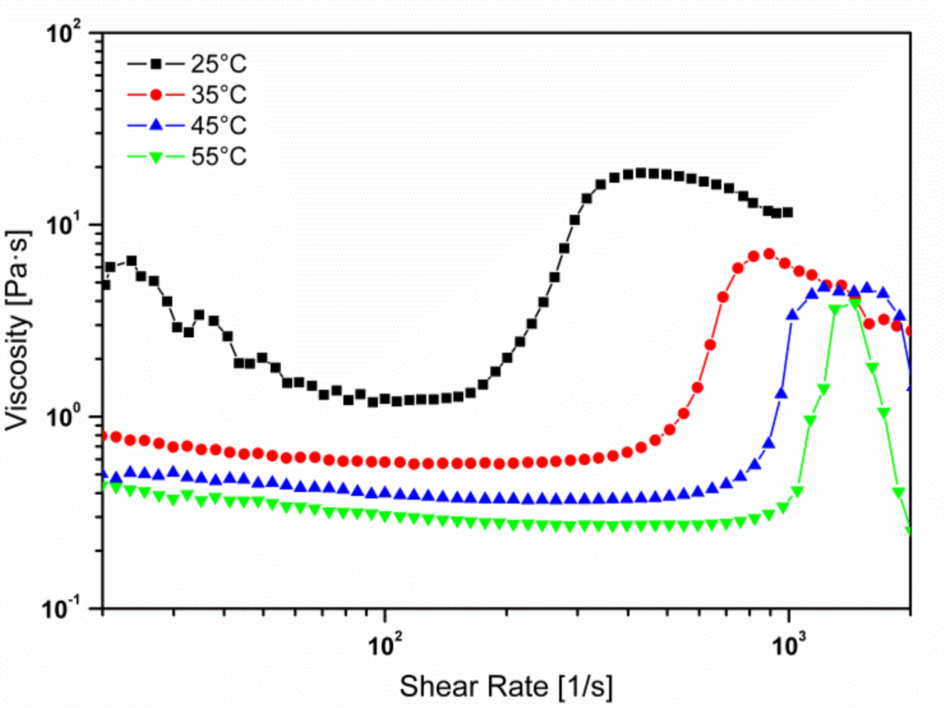


Figure 6.3 Steady-state rheology of 20% STF with different add-on concentration of nanoclay.

Besides, the influence on shear thickening properties, the amount of additives affects the rheology of STF at different temperatures in an interesting way as shown in Figure 6.4. The experiments were also done at 35^0, 45^0, and 55^0C, to study the effect of temperature on STF behavior for 3 and 5 phr concentration. As the temperature increases, the strength of hydrogen bonding between the particles and PEG molecules decreases and the Brownian forces increases. These results in a decrease in low shear viscosity and increase in repulsive forces, resulting in the requirement of higher shear rates for formation of hydroclusters. Hence an increase in temperature results in a decrease in critical viscosity and an increase in critical shear rate values. This is consistent with results reported in the literature [3, 5, 8, 9] and also in chapter 5. It is noted that there is a large decrease in viscosity values for 3 phr of both additives (Figures 6.4a and 6.4b) as compared to their 5 phr concentration at all the temperature studied (Figures 6.4c and 6.4d). Additionally, it turns out that the 3 phr clay as nano-filler makes the STF retain the high value of viscosity over a large range of shear rates as indicated by a gradual decrease (broad shoulder) in viscosity after the critical viscosity (Figure 6.4b). Significantly, at high temperatures of 45^0 and 55^0C, the further decrease in viscosity values becomes negligible for clay as additive as shown in Figures 6.4b and 6.4d i.e. addition of clay decrease the effect of high temperature and prevent the decrease in viscosity at higher temperatures. Still, higher temperatures were not studied as the samples would eject out from the rheometer plate due to very low viscosity in the course of the experiment, and also because at temperature exceeding 55^0C, the critical viscosity values are too low for any possible application.

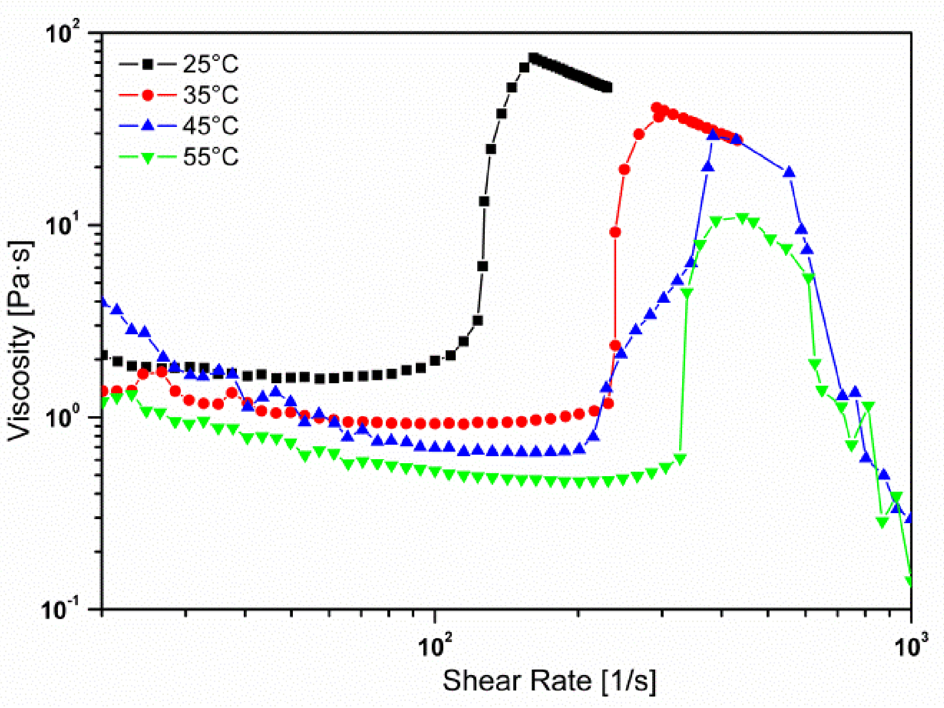


(a)



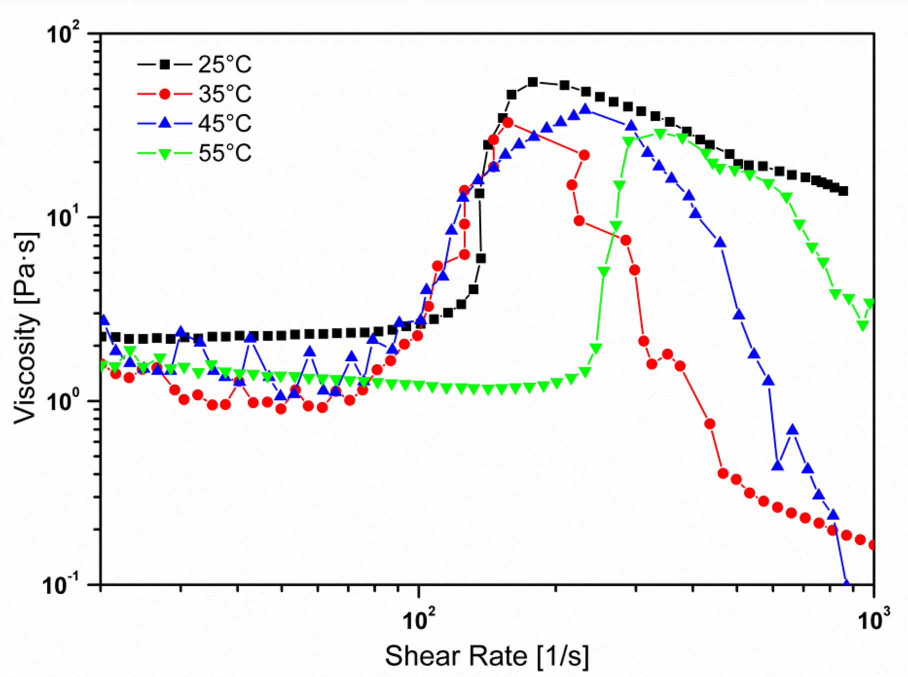
25°C
35°C
45°C
55°C
Viscosity [Pa·s]
Shear Rate [1/s]
10^{2}
10^{1}
10^{0}
10^{-1}
10^{2}
10^{3}

(b)



25°C
35°C
45°C
55°C
Viscosity [Pa·s]
Shear Rate [1/s]
10^{2}
10^{1}
10^{0}
10^{-1}
10^{2}
10^{3}

(c)



(d)

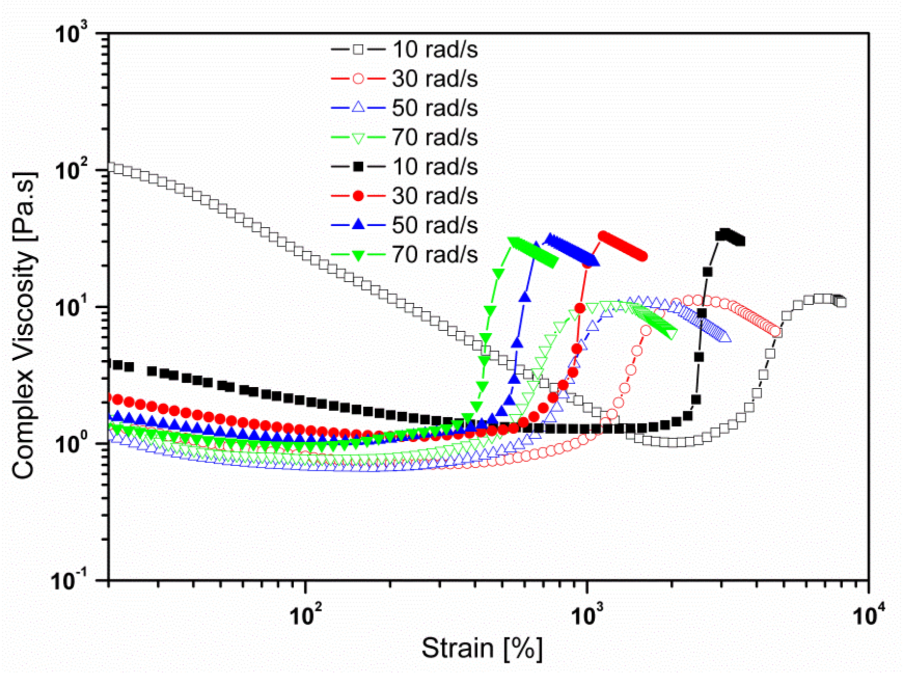
Figure 6.4 Steady-state rheology of 20% STF as a base containing (a) 3 phr fumed silica (b) 3 phr nanomer (c) 5 phr fumed silica and (d) 5 phr nanomer as filler.

6.3.2 Dynamic state rheology

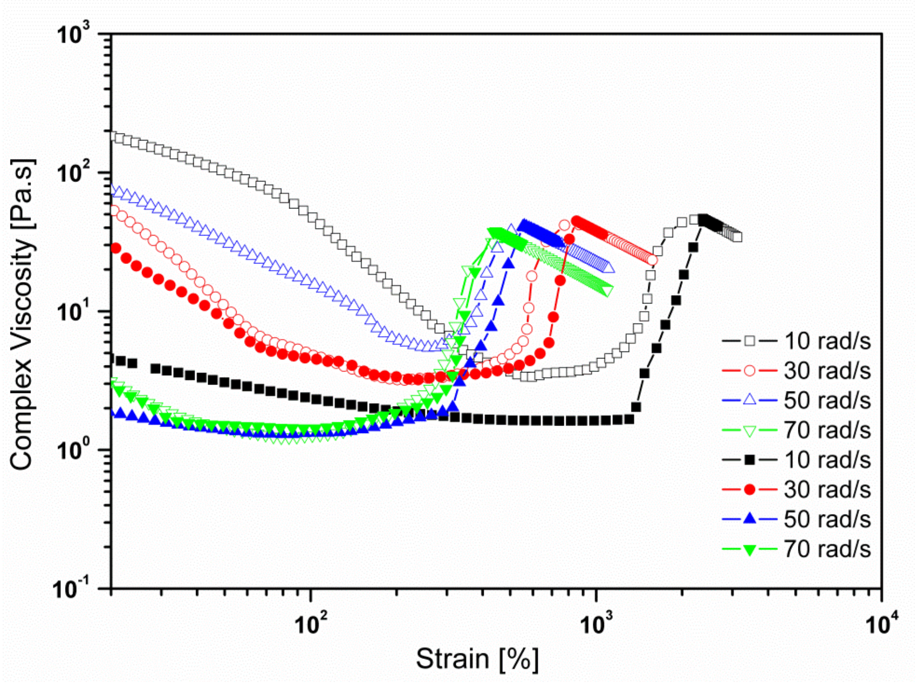
The dynamic rheological results at 25^0C with respect to the complex viscosity at different constant frequencies shown in Figure 6.5 depict strain thickening behavior of STF after critical strain. It can also be seen that this transition occurs at smaller strains as the constant value of the frequency of deformation is increased and the critical value of complex viscosity decreases slightly. This agrees well with the results reported in Chapter 5 and in the literature [10, 11]. The reason for this may be that at high frequency small strain is sufficient to form hydroclusters and subsequently, the less time is available for particles to form large size hydro clusters which result in a decrease in critical value of complex viscosity. Interestingly, for clay nanoparticles as additives, the change in critical value of steady-state (Figure 6.3) and complex viscosity (Figure 6.5) at both 3 and 5 phr concentration is negligible but for nano-silica, at higher concentration of phr, the critical value of the steady state viscosity (about 74 Pas) is consistently higher than the critical value of complex viscosity (about 60 Pas). The probable reason is that the particle-

particle interaction for fumed silica particles would be predominantly higher under steady-state than in dynamic state conditions. In dynamic state continuous forming and breaking of fumed silica particle clusters would prevent viscosity buildup with consistently greater effect for higher loading. Also, it can be noted from Figure 6.5b that the complex viscosity of both 5 phr nanomer and 5 phr fumed silica are almost the same. This concluded that in contrast to steady-state deformation, under dynamic-state deformation at same high concentration, both fumed silica and nanomer as additive show similar shear thickening properties. Similar to steady state critical shear rate, the critical strain also depends only on the concentration of additive at all frequencies studied except at very low frequency of 10 rad/s. This suggests that at a very low frequency, high strain percent is required for shear thickening.

Also expectedly, the values of storage and loss modulus increases as the concentration of fillers increase with a sudden upturn at the critical strain. From Figures 6.6 and 6.7, it can be seen that in strain sweep at all four frequencies studied, G' and G'' show three zones similar to the complex viscosity profile i.e. as strain increases initially, G' sharply decreases whereas, G'' decreases slightly and then increase due to increase in cluster volume. G' values drop at higher strains, as a result of rupture of clusters (Figure 6.6), suggesting the relaxation of the structures of STF. G'' also decreases due to collapsing of the clusters resulting in strain thinning (Figure 6.7). However, as the constant frequency value increases, the critical value of G' and G'' increases, which again confirms that on shearing suspension more quickly, it become more elastic and viscous.

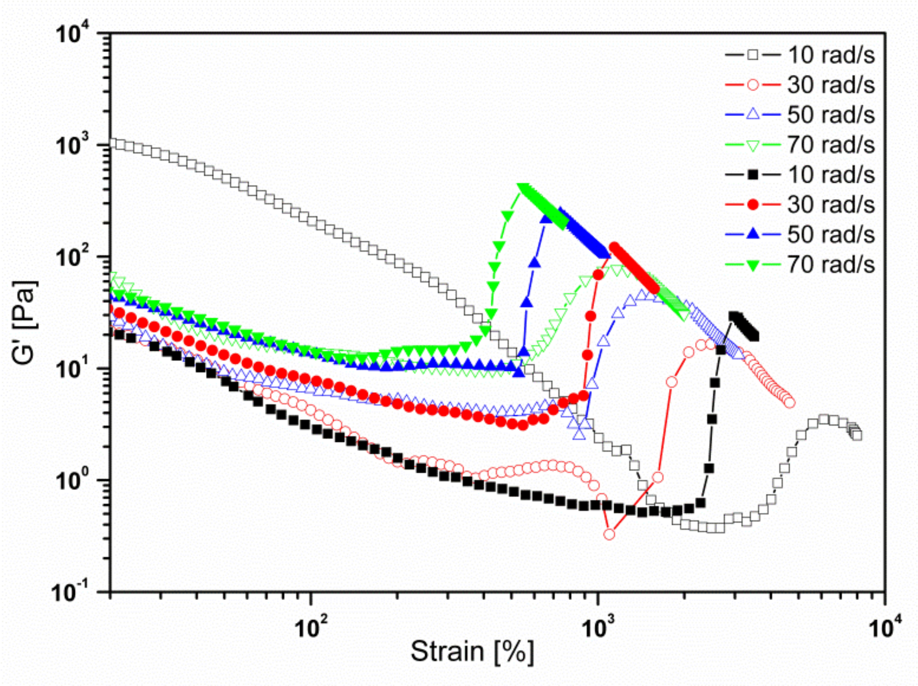


(a)

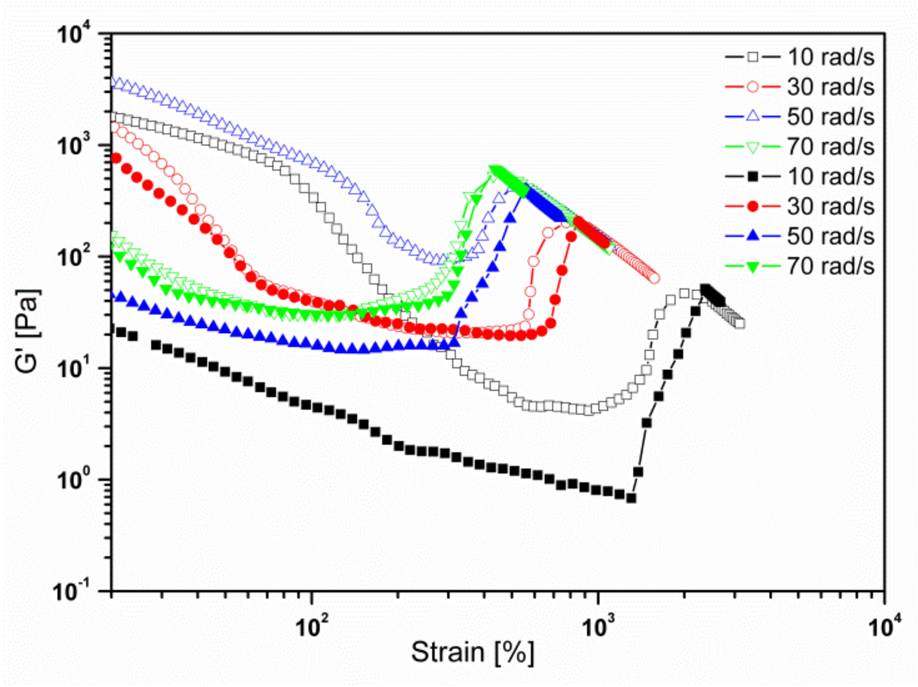


(b)

Figure 6.5 Comparison of complex viscosity at different frequencies a) 3 phr nanomer (open symbols) and fumed silica (closed symbols) b) 5 phr nanomer (open symbols) and fumed silica (closed symbols).

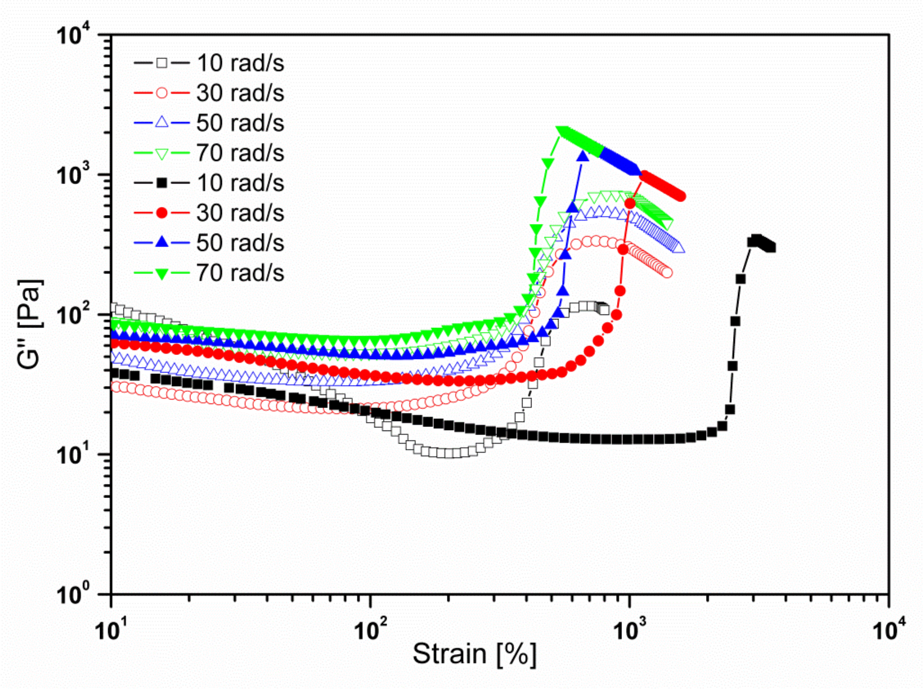


(a)

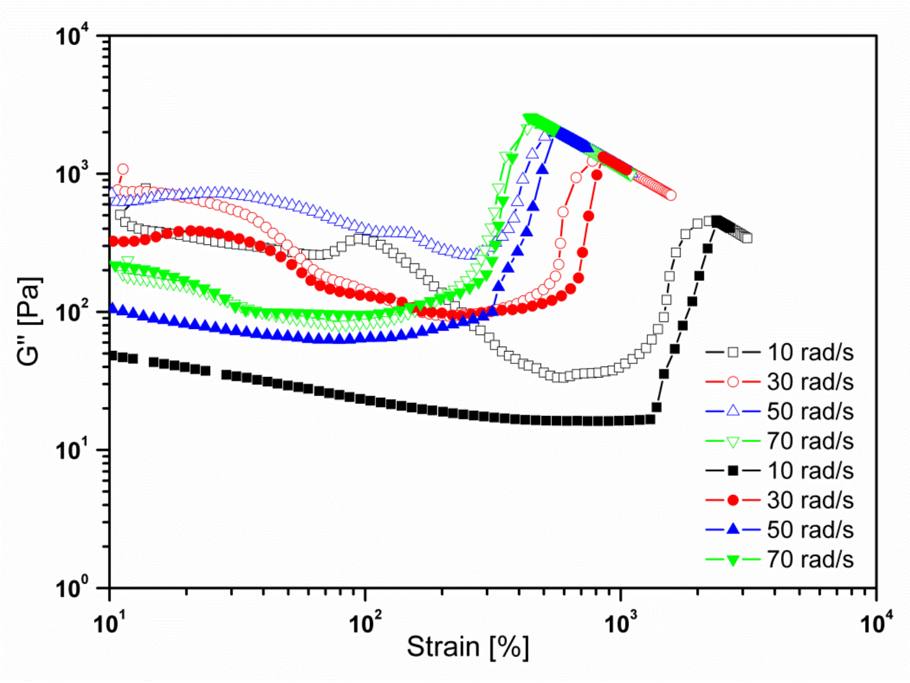


(b)

Figure 6.6 Comparison of storage modulus at different frequencies a) 3 phr nanomer (open symbols) and fumed silica (closed symbols) b) 5 phr nanomer (open symbols) and fumed silica (closed symbols).



(a)



(b)

Figure 6.7 Comparison of loss modulus at different frequencies a) 3 phr nanomer (open symbols) and fumed silica (closed symbols) b) 5 phr nanomer (open symbols) and fumed silica (closed symbols).

The general appearance of these plots (Figures 6.6 and 6.7) are similar, with the plots of the more concentrated samples start to fall at lower strains. It has also been noted that the elastic modulus *G'*, is more sensitive to shear strain than the loss modulus, *G"*, and shows a highly non-linear response. Add on percentage of 3 phr of both additives (Figures 6.6a and 6.7a) gives smooth curves of *G'* and *G"* with strain percentage increases while a sharp increase in moduli is noted for 5 phr (Figures 6.6b and 6.7b). *G'* and *G"* increase at a high rate as frequency increases from 10 to 30 rad/s but as frequency increases from 50-70 rad/s, the rate of increase, decreases such that there is very less difference in critical values of *G'* and *G"*. Also, viscous properties are always more for 5 phr nanomer as the additive but in case of fumed silica as nano-additive there is negligible change in values as compared to 3 phr in spite of an increase in values of complex viscosity at low shear rates. *G'* describes the structure of system i.e *G'*>*G"* indicates well structured or gelled system and *G'*<*G"* shows a weakly structured system. For the STF studied, as *G"*>*G'*, therefore STF are viscoelastic fluids. Thus, STF shows a striking non-linear suspension like response as the strain deformation is increased. High frequency and low frequency corresponds to the rate of deformation same as at faster impact and slower impact at very high deformation time, respectively.

6.3.3 Stability

Clay is known to have a high settling tendency in suspensions. However, in the present study all compositions of STF were stable for more than a month and no phase separation was seen. There was however a decrease in values of viscosities. For reproducible results and consistent performance, the STF should be stable for a reasonably long time period i.e dispersed particles should not agglomerate. Over the time period of one month, it was also noted that at low concentration of 3 phr nanoclay as an additive, a small amount of deposition of clay was seen however interestingly for a high concentration of nanoclay (4 and 5 phr), no settling was observed. This may be attributed to the possible high intercalation of PEG molecules in the interlayer spacing of this swelling clay which is more for high concentration compared to low concentration, that compatablizes the clay particles and prevent their settling. Additionally, it is very interesting to note that on repeating the same experiment thrice, STF containing clay as additive gave more reproducible results than fumed-silica STF without clay.

6.4 Conclusion

The present study demonstrates the development of relatively inexpensive STF of fumed silica-PEG with nanomer clay as an additive. Then STF were compared with the same overall concentration of only fumed silica STF. Clay and fumed silica both contain silica but clay is relatively cheaper than silica and also is eco-friendly, and these factors will remain one of the primary advantages for using clay-based additives over fumed silica as well as spherical silica and other particles in shear thickening fluids in future. From the steady-shear experiments, it can be concluded that the addition of additives doesn't change critical shear rate but increases critical viscosity significantly. One of the advantages of clay is that high strain rates are typically sustained for much longer times, also it takes time for many damage mechanisms to develop. Importantly, clay makes the STF less sensitive to increase in temperature. Clay as nano-additive gives the same value of maximum viscosity in both the steady-state and dynamic state. Complex viscosity and both moduli increases as frequency and concentration increase for clay as nano-additive but the critical value of all parameters remain almost the same as the concentration of fumed silica increases. Thus, in contrast to fumed silica as additive, nanoclay as filler increases both viscous and elastic nature. Most importantly clay as nano-additive shows more stability and reproducible/consistent results. It was also established that the nano-particle shape matters and it is not simply the total percentage of solid particles in STF which determines the rheology.

Thus, the importance and advantage of using nanoclay as an additive are clearly seen. It can be inferred that the amount of clay must be chosen judiciously to achieve the desired shear thickening behavior and impact resistance performance of STF to be used for various protective applications.

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Chapter 7 Effect of addition of alumina particles to 20% fumed silica-PEG STF

The STF showed enhanced shear thickening properties by addition of different clay additives as studied in previous Chapters 4, 5 and 6. Further, the study of the potential of alumina oxide as an additive for reference STF and differentiating it with clay as additives were done in this chapter.

7.1 Introduction

Apart from nano-silica and clay particles, there are many types of nano-materials: CNTs, graphene, metal oxides etc. as some of the materials are a hazard from environmental concerns combined with their high cost due to less availability making them less attractive for large-scale applications [1-5].

In this chapter, alumina nano-particles as nano-additives in the fumed-silica-PEG STF have been studied. Alumina is a pure oxide in contrast to clays which are alumino-silicates and having high aspect ratio [6]. The present study reports some surprising observations on the effective shear thickening properties due to the addition of pure oxide as an additive while trying to investigate the effect of concentration, temperature, shear rate, shear strain, and frequency. Alumina nanoparticles have a hydrophilic surface with hydroxyl ions and thus have a negative surface charge. Alumina nanoparticles can’t be used alone as dispersed particles with PEG as they have a) high chemical activity b) high surface area, and c) possesses high surface energies. Thus they have a tendency to form aggregates to minimize the surface energy resulting in flocculated sol with shear thinning properties. However, addition of a small amount of alumina with silica particles should minimize the aggregation of nanoparticles due to polydispersity resulting in a decrease in attractive forces. Moreover, the organic chains of the polymer adsorbed on the surface of the nanoparticles should also prevent the formation of attractive oxygen bridge bonds and obstruct the agglomeration of particles [7-9]. Thus, the strategy comprises of adding a minimum amount of alumina particles that can be charge stabilized by the given amount of the silica particles.

7.2 Processing

Alumina particles are firstly dispersed in polymer PEG by ultrasonication and subsequently, silica nanoparticles were added to the dispersed alumina particle suspension. 3 and 5 phr were selected as minimum and maximum concentration based on our preliminary tests. Rheological studies were conducted after removing air bubbles trapped in the samples by subjecting the samples to vacuum for 12 h.

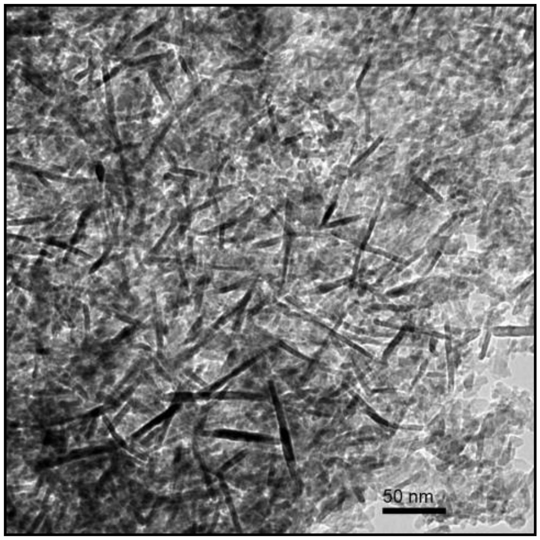


Figure 7.1 TEM image of alumina particles (Sigma Aldrich)

7.3 Results and discussion

7.3.1 Steady-state rheology

Steady-state viscosity profiles for Alumina particles as additives are shown in Figure 7.2 as viscosity versus shear rate plots highlighting shear thickening behavior for silica-alumina suspensions in PEG with 3 and 5 phr concentrations of alumina particles. At low shear rates STF show shear thinning behavior and at sufficiently high shear rates, shear thickening occurs. The high shear thickening behavior is attributed to the tubular shape and lamellar morphology of the alumina particles along with the shear thickening properties of fumed silica STF. The critical viscosity achieved for 3 phr concentration of alumina (22 Pa.s) is more than that of MMT clay

(11 Pa.s) and comparable to that of nanomer clay (21 Pa.s) as additive. However, critical shear rate value is high than that of nanomer clay as additive. For the 3 phr concentration of alumina particles, shear thickening is obtained after a shear rate of 250 s^{-1} and critical viscosity is 22 Pa.s. Adding 5 phr alumina particles increase overall viscosity values, however, it does not increase the critical viscosity but critical shear rate decrease to 150 s^{-1}. As for 5 phr concentration viscosity values at low shear rates are high thus, overall shear thickening rate is less.

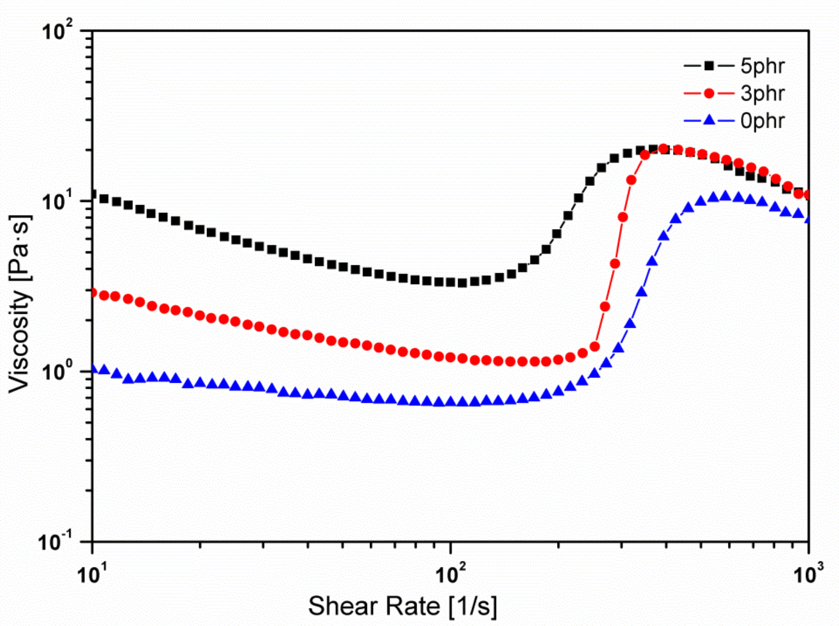
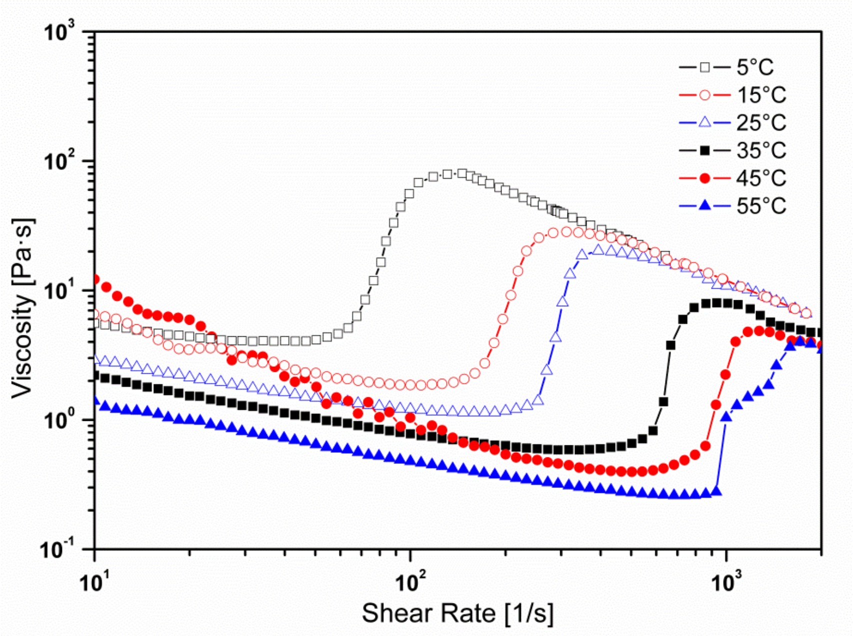
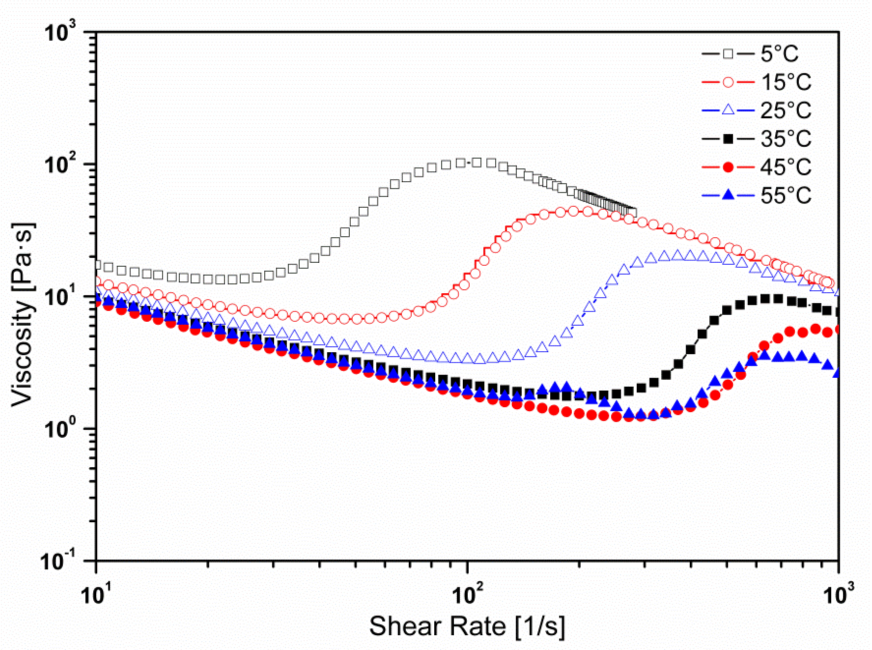


Figure 7.2 Steady-state viscosity profile of 0, 3 and 5 phr concentration of alumina particles as an additive in 20% fumed silica-PEG STF



(a)



(b)

Figure 7.3 Steady-state viscosity profiles of a) 3 phr and b) 5 phr concentration of alumina particles as an additive in 20% fumed silica-PEG STF at different temperatures.

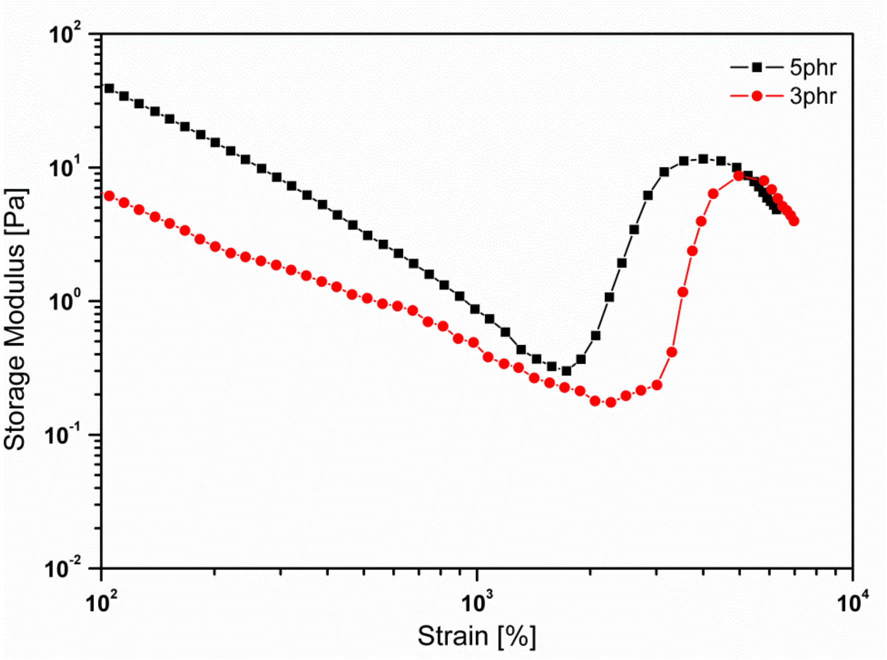
It is expected that extra amount (>3 phr) of alumina particles causes its initial flocculation. As for high concentration of alumina particles, silica particles will be less to interact with all the alumina particles. Thus, it eliminates the contribution of particles in increasing the critical viscosity and decreases the critical shear rate value by half.

Rheological studies at different temperatures for 3 phr and 5 phr concentration are shown in Figure 7.3a and 7.3b respectively. It is concluded from Figure 7.3a that from 25^0C to 5^0C decrease and from 20^0C to 55^0C rise in temperature the critical viscosity values increases by 4 times (22 to 80 Pas) and decreases to 4 times (22 to 5 Pas) respectively for 3 phr concentration. However, critical shear rate values decrease to 4 times from 200 to 50 s^{-1} when temperature decreases from 20^0C to 5^0C and increases to 5 times (200-1000 s^{-1}) from 20^0C to 55^0C. Similarly, for 5 phr concentration, as depicted by Figure 7.3b an increase in critical viscosity value from 22 to 105 Pas (about 5 times) on decreasing temperature to 5^0C and decrease to 3 Pas (about 7 times) on increasing temperature to 55^0C. Moreover critical shear rate values decrease to 3 times (100 to 30 s^{-1}) on the lower temperature side and increase to 3 times (100 to 300 s^{-1}) on the higher temperature side. Therefore it can be concluded that 3 phr show less change in critical viscosity values with respect to temperature compared to 5 phr concentration.

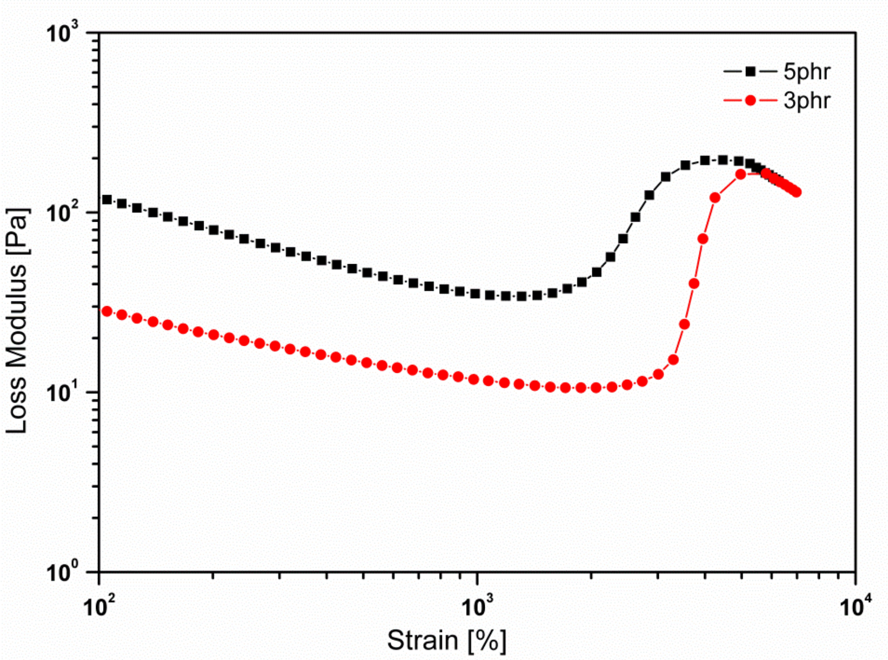
7.3.2 Dynamic-state rheology

The dynamic study can adequately predict the important information on the general form of flow curves under high strains by introducing values of complex viscosity, loss modulus, and storage modulus.

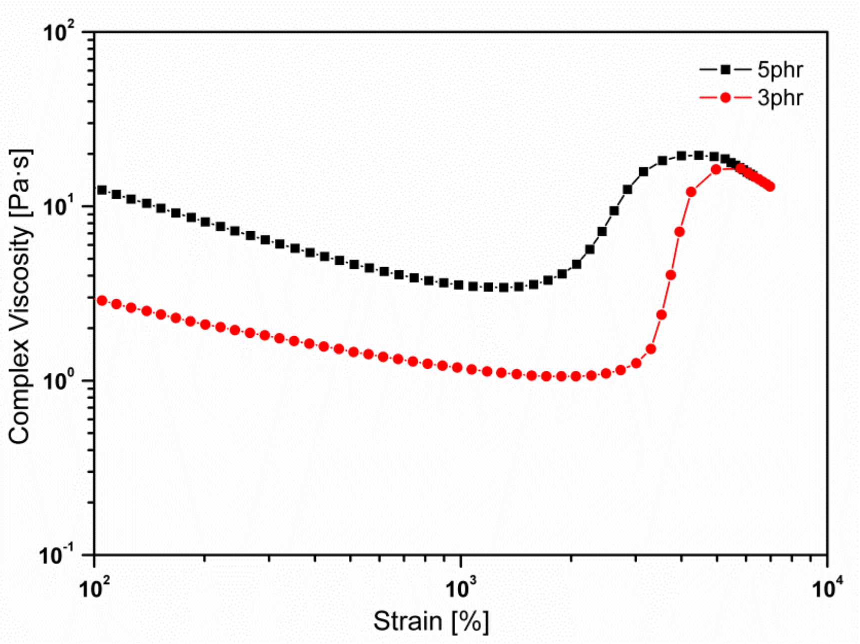
Dynamic state parameters (storage modulus, loss modulus, and complex viscosity) at 10 rad/s is shown in Figure 7.4. The increase in storage modulus (Figure 7.4a) values at initial strains to that of values after critical strain for both the concentration is approximately the same. However, there are about 15 times increase in loss modulus and critical viscosity values after critical strain from that of the values at initial strains for 3 phr concentration as compared to only 5 times increase for 5 phr concentration (Figure 7.4b and Figure 7.4c). The critical viscosity data shown in Figure 7.4c matched well for both 3 and 5 phr concentration to that of the steady-state profile.


Storage Modulus [Pa]
Strain [%]
5phr
3phr
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{2}
10^{3}
10^{4}

(a)


Loss Modulus [Pa]
Strain [%]
5phr
3phr
10^{3}
10^{2}
10^{1}
10^{0}
10^{2}
10^{3}
10^{4}

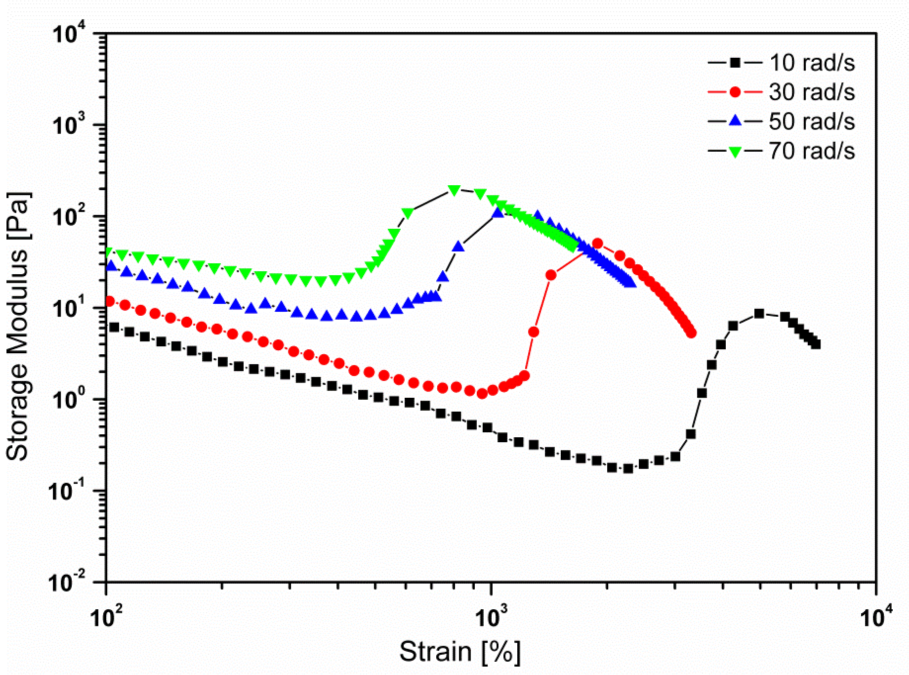
(b)



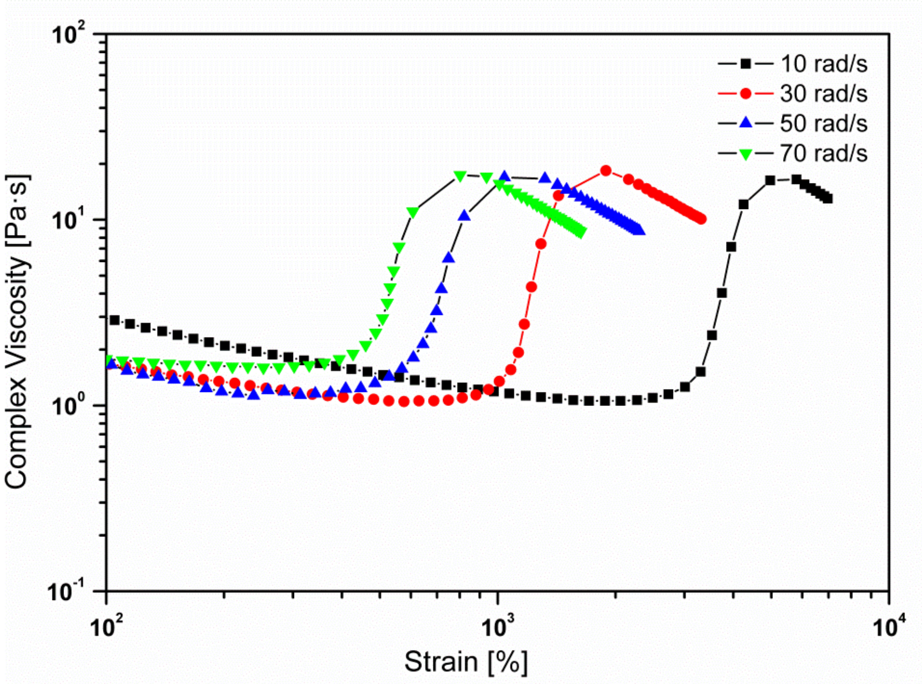
(c)

Figure 7.4 Dynamic-state rheology profiles of a) storage modulus b) loss modulus and c) complex viscosity for alumina particles as additives at 10 rad/s

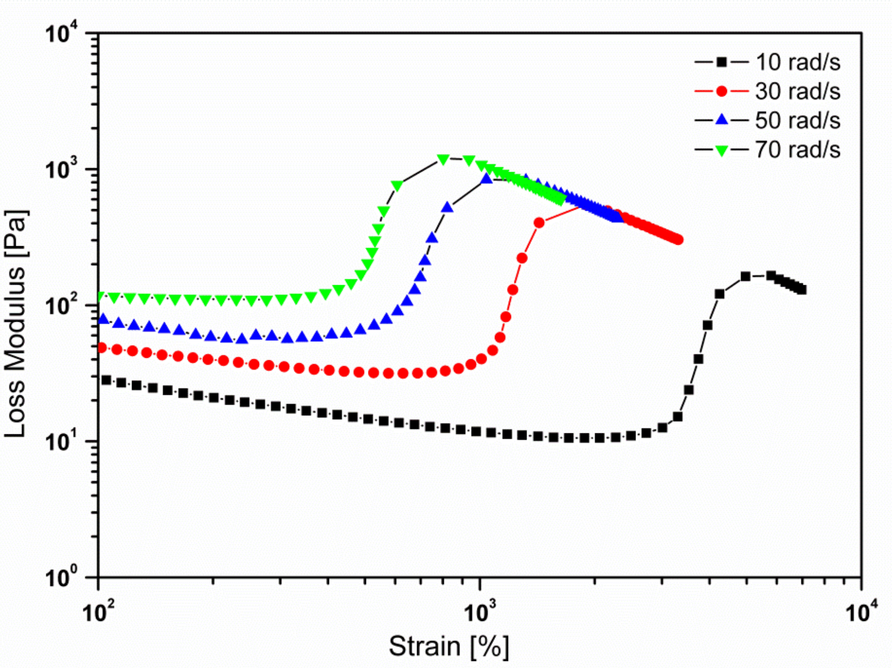
Thus, it can be concluded that 3 phr of alumina is the optimum concentration with a higher rate of shear thickening behavior, less change with respect to temperature and higher viscous properties and comparable elasticity to that of 5 phr concentration. Further, 3 phr and 5 phr concentration is compared in dynamic state under different constant frequency values of 10, 30, 50 and 70 rad/s. From Figure 7.5 it can be seen that for 3 phr concentration on increasing frequency, both moduli increases and the value of critical strain decreases a lot. On contrary, there is no effect of the increase in frequency on the critical values of complex viscosity. The probable reason for this behavior as also discussed in previous chapters is that at high frequencies the 3-D network of STF did not have time to be fully broken hence at even low critical strain start to form hydroclusters and that too of large sizes.


10 rad/s
30 rad/s
50 rad/s
70 rad/s
Storage Modulus [Pa]
Strain [%]
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^2
10^3
10^4

(a)

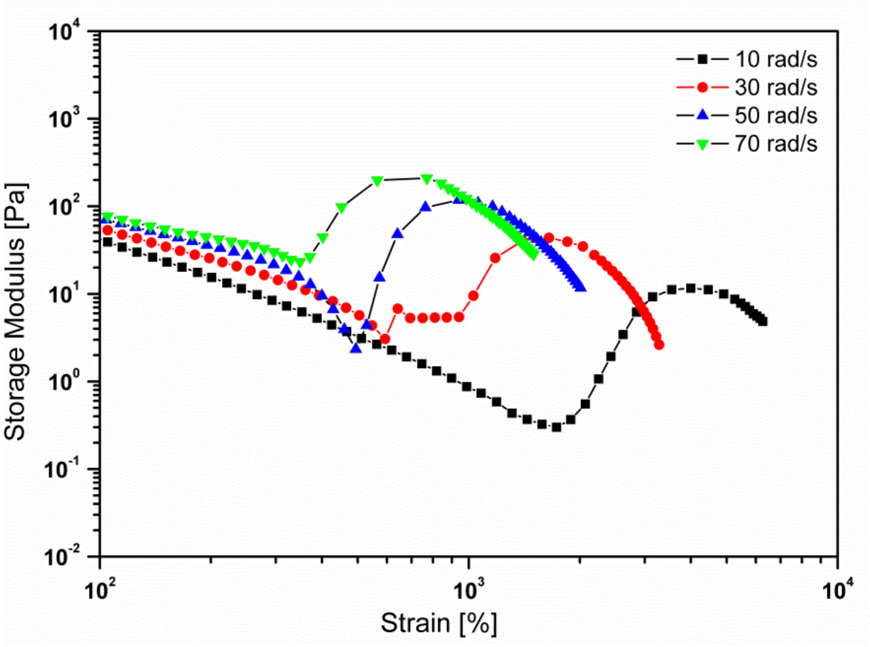

10 rad/s
30 rad/s
50 rad/s
70 rad/s
Complex Viscosity [Pa·s]
Strain [%]
10^2
10^1
10^0
10^{-1}
10^2
10^3
10^4

(b)

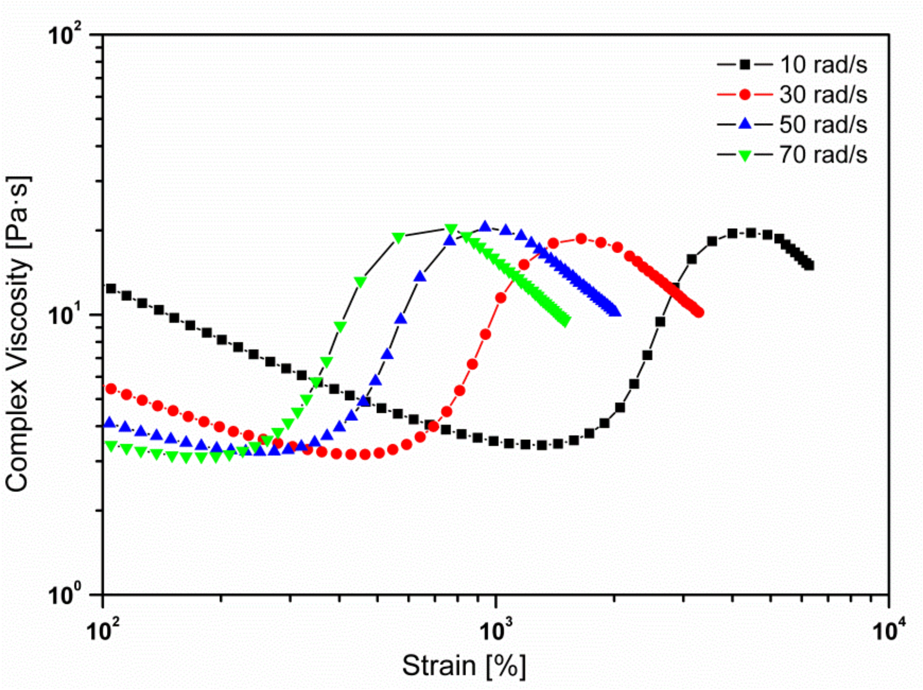


(c)

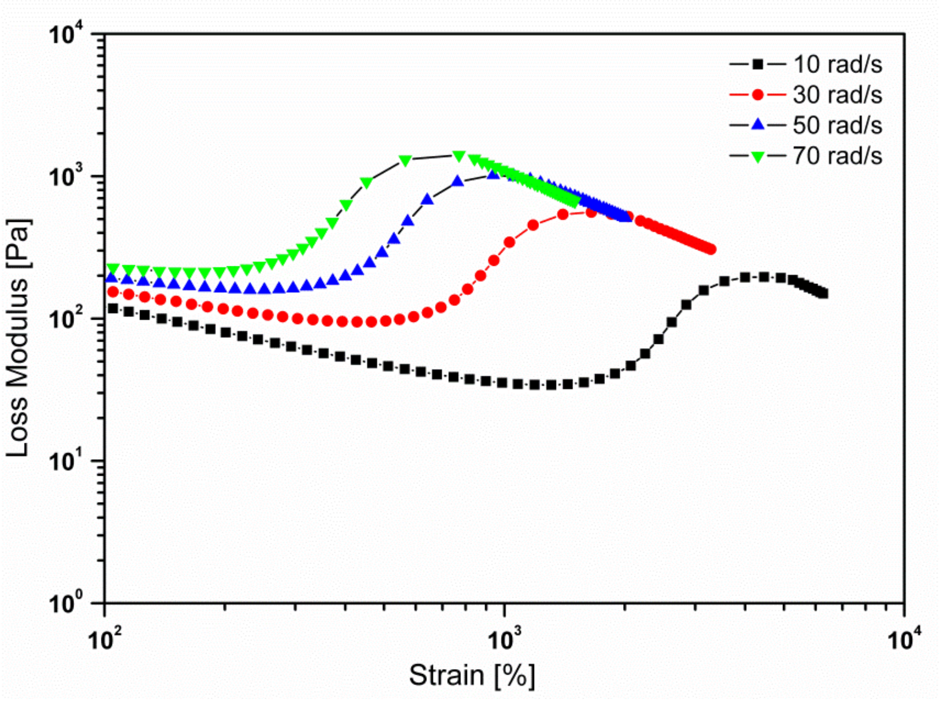
Figure 7.5 Strain sweep profiles of a) storage modulus b) complex viscosity and c) loss modulus of 3 phr alumina particles as an additive at different frequencies



(a)



(b)

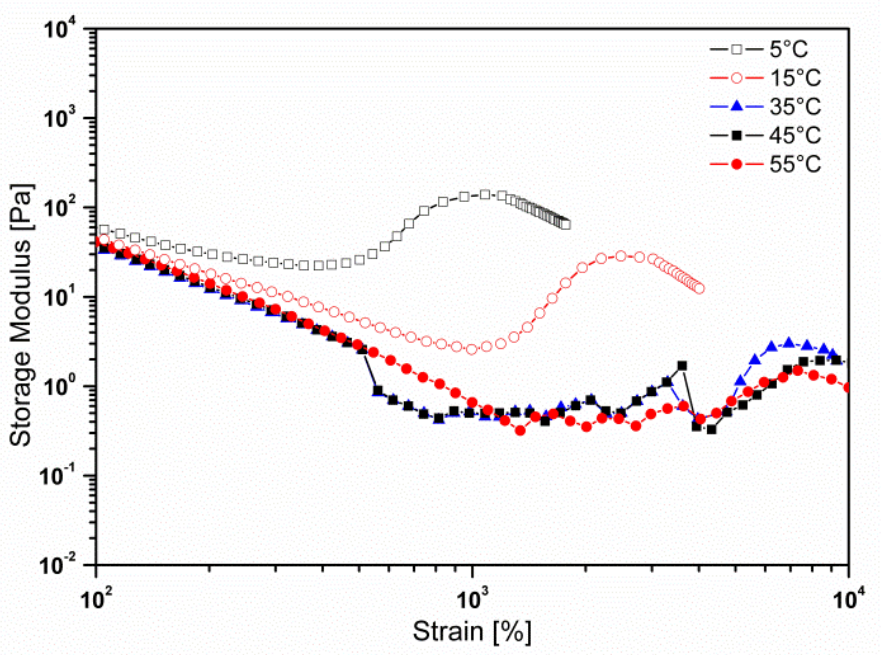


(c)

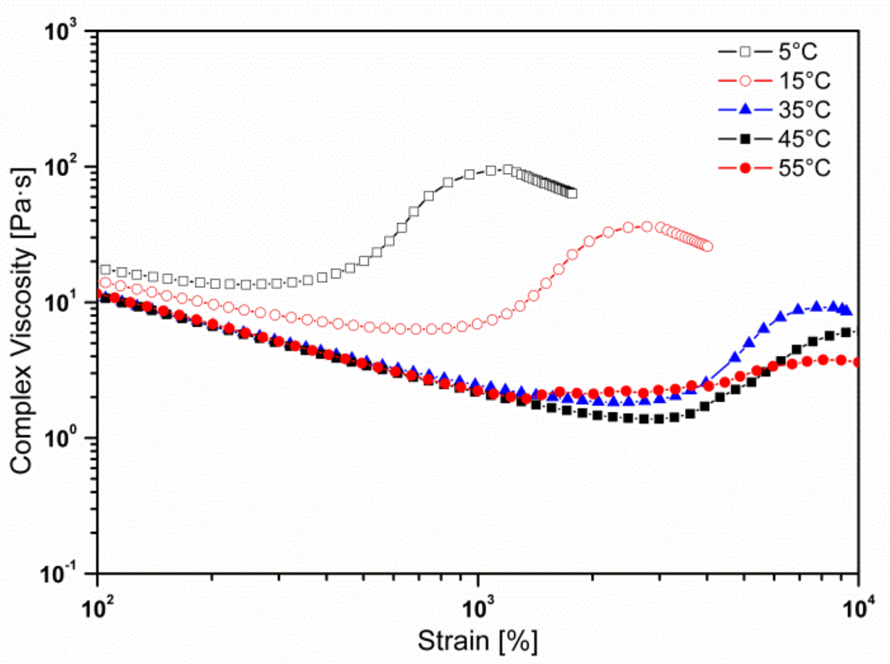
Figure 7.6 Strain sweep profiles of a) storage modulus b) complex viscosity and c) loss modulus of 5 phr alumina particles as an additive at different frequencies

From Figure 7.6, again similar behavior to that of 3 phr concentration is observed for the 5phr concentration of alumina particles. However, for 5 phr concentration, the increase in parameters is not smooth when compared with 3 phr concentration. This behavior again confirms that 3phr concentration is more stable than 5 phr concentration.

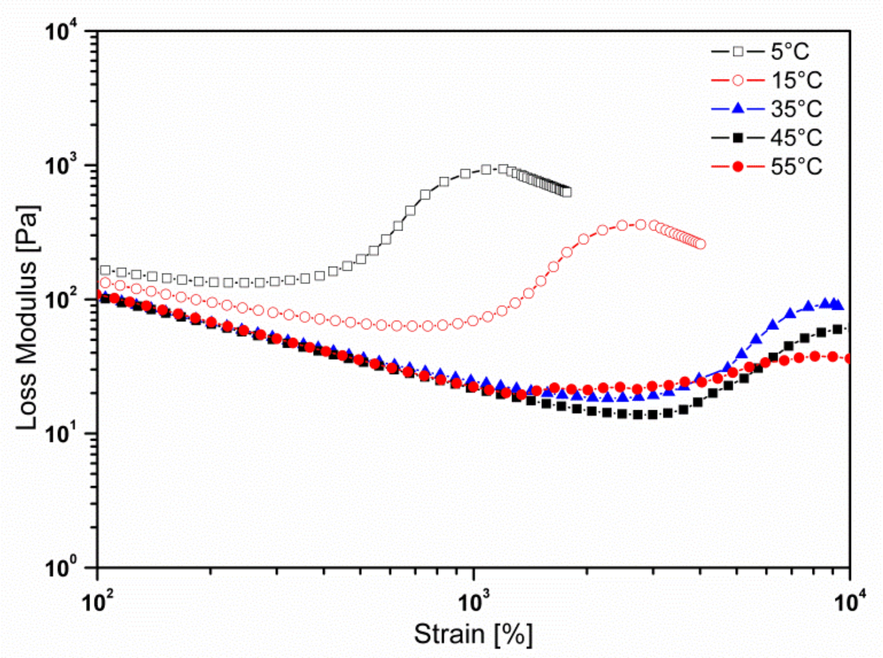
As 3 phr concentration appeared as optimum concentration therefore for this concentration dynamic rheology at different temperatures were also studied. From dynamic-state rheology at different temperatures (Figure 7.7) for 3 phr concentration, it can be concluded that in the range 35^0C to 55^0, all the dynamic parameters show very less critical values whereas at lower temperatures (5^0C to 15^0C), the values of these parameters after a critical strain, increases a lot.



(a)

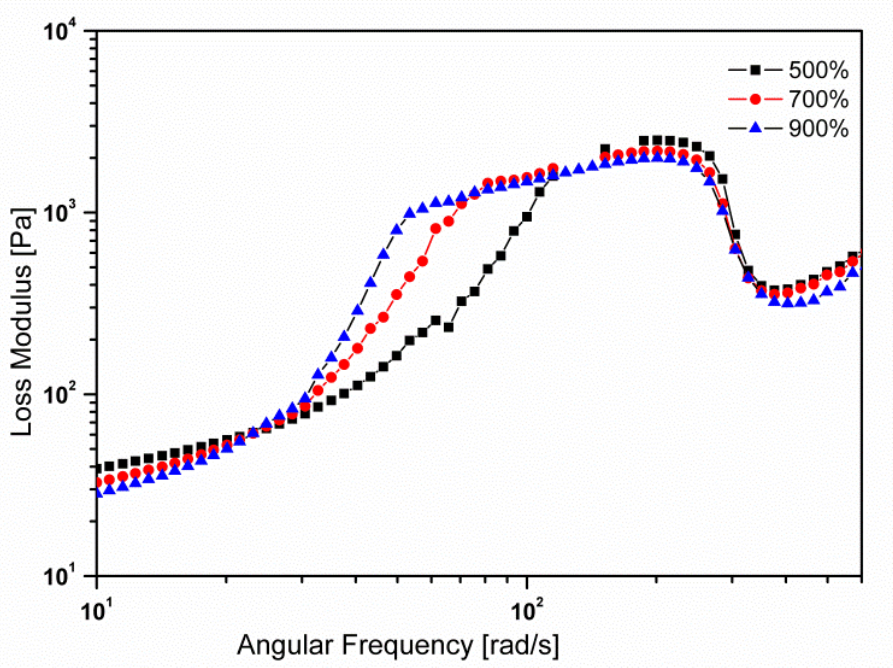


(b)



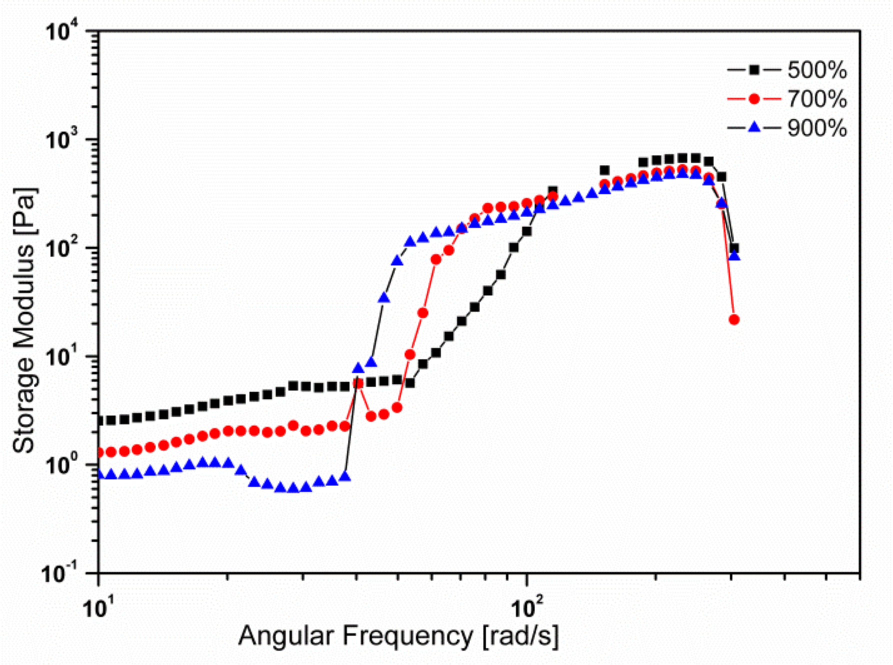
(c)

Figure 7.7 Strain sweep profiles for 3 phr alumina particles as additives at 10 rad/s at different temperatures



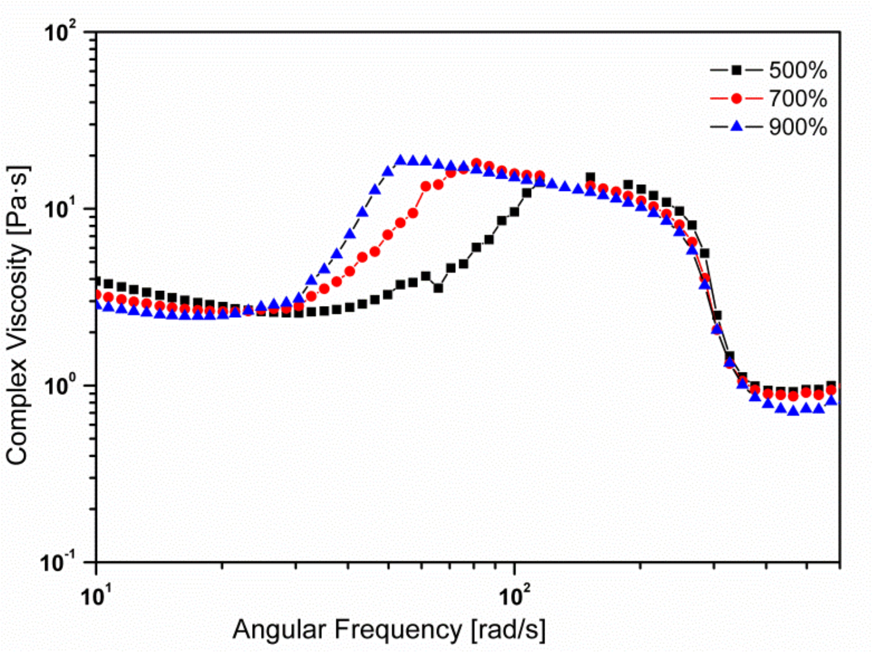
Loss Modulus [Pa]
Angular Frequency [rad/s]
10^4
10^3
10^2
10^1
10^1
10^2
500%
700%
900%

(a)



Storage Modulus [Pa]
Angular Frequency [rad/s]
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^1
10^2
500%
700%
900%

(b)



(c)

Figure 7.8 Frequency sweep profiles of a) loss modulus b) storage modulus and c) complex viscosity for 3 phr alumina particles as additives at different strains

Frequency sweep profiles for 3 phr concentration at different constant strains of 500%, 700%, and 900% are shown in Figure 7.8. Dynamic state parameters show a sharp increase after critical frequency for high values of constant strain. Additionally, at high frequencies a plateau region is obtained which indicates that both moduli become independent of frequency which is a characteristic of a solid nature. Additionally, the value of frequency after which parameters become independent of frequency increases as the value of constant strain decreases. At further high frequencies, a rupture of the solid structure starts resulting in a steep decrease in values of all dynamic parameters.

7.4 Conclusion

The alumina as additive, shows much higher shear thickening compared with when reference STF of only fumed silica and STF contain MMT clay as an additive. Interestingly, alumina particles as additives show high values of both the moduli than MMT clay, may be due to high plasticity of the clay which makes STF with clay, soft under high strains. However, compared to all other clays critical values of STF with alumina as an additive is about 10 times less. Increase in concentration of alumina particles from 3 to 5 phr, does not result in an increase in critical viscosity but critical shear rate decreases. Thus, Alumina particles at a low concentration only can modify the shear thickening properties. However, overall aluminosilicates i.e. clay perform superior to that of pure oxide (alumina). From this study, very important conclusion can be drawn that the additives to be used for enhancing shear thickening properties should have compatibility with fumed silica particles as aluminosilicates are more compatible with silica particles than the pure oxide of alumina.

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Chapter 8 Polyethylene glycol of different molecular weight as additives

As discussed in Chapter 3, high molecular weight PEGs show crosslinking properties, therefore, in this chapter, the steady-shear viscosity and dynamic visco-elastic behavior of suspensions of 20 weight % fumed silica-PEG200 STF with different concentrations of various molecular weight PEGs (4600, 6000 and 10000) has been studied. The results demonstrate that the shear thickening parameters are significantly enhanced with an increase in the molecular weight of PEG used as an additive to base dispersing medium. In steady-state rheology, the addition of PEG6000 as an additive result in high shear thickening at both low and high temperatures whereas, in the dynamic state, PEG4600 gives high values of all dynamic parameters. Additionally, the ability of the long polymer to interconnect several fumed silica particles, acting as cross-links explains the mechanism of the enhancement in viscosity. However, compositions having PEG10000 as additive exhibits shear-thinning rheology. Long polymer chains increase hydrodynamic forces thus aggregation of particles increases. Also, the results demonstrate the effect of high molecular weight PEGs on the elasticity and stability of the STF, which is important with regard to high impact resisting applications.

This study is based on: Effect of molecular weight of polyethylene glycol on the rheological properties of fumed silica-polyethylene glycol shear thickening fluid; Mansi Singh, Sanjeev K Verma, Ipsita Biswas and Rajeev Mehta; Material Research Express, DOI: 10.1088/2053-1591/aac25c/meta

8.1 Introduction

The results of Chapter 5 showed that for tailoring the shear thickening properties i.e. critical shear rate and critical viscosity, different additives like different nanoclays of high aspect ratio can be used [1]. Analogously, different fluids such as viscoelastic polymers, in particular, ethylene glycol, polypropylene glycol and silicone oil having a highly branched structure can also enhance shear thickening behavior [2-4]. The study done by Raghvan [5] concluded that strong hydrogen bonding (polar) liquids like lower glycols and n-alkanols form stable sol with silica particles due to solvation layer whereas weakly hydrogen bonding liquids lead to gel formation due to particle-particle bonds. Also, it has been reported by Antosik et al [6] that chain length, hydroxyl groups and oxygen atoms of fluids strongly influence the rheological properties of shear thickening suspensions.

Generally, polymers are viscoelastic in nature i.e. have elastic properties along with viscous properties provided by the long chain molecules during deformation [6]. Also, some studies have confirmed that these visco-elastic materials can absorb the energy of impact [7]. High molecular weight PEG is generally considered as a thickening or gel-forming agent and appears to possess at least some hydrophobic nature. These are relatively inert polymers with a large excluded volume and are amphiphilic i.e. in solution they display characteristic molecular self-assembly behavior due to the presence of both hydrophobic and hydrophilic character. Therefore, PEG with molecular weight >1000 forms random coils and molecular weight <600 form stretched aggregated chains in solution [8, 9]. Table 8.1 shows the properties of different molecular weight PEG [10]. High molecular weight PEG molecules tend to agglomerate at a lower temperature hence can only be dissolved at high temperature (> 60^0C) [11]. It has been reported that high molecular weight PEG acts as an effective flocculant for hydrophobic substances but for silica particles (hydrophilic) it offers a stable suspension [12, 13]. High molecular weight PEG due to large molecules form tails and loops and are more amenable to the formation of bridging flocculation (weak interaction broken by vigorous stirring) at high concentration [14]. Nevertheless, PEG is a popular and best synthetic non-fouling material with unique properties like a high degree of hydrophilicity; a high extent of coordination with surrounding liquid molecules and high level of chain mobility.

Low molecular weight PEG (PEG200-1000) is more mobile and hygroscopic. They are thought to penetrate more deeply into the fibrils and porous media when used in a STF for intercalation with protective fabrics. However, if too much of it is used, the surface of the fabric would look wet, attract dust, and be sensitive to humidity. Whereas, high molecular weight PEG (PEG 1500-10000) will not penetrate into the fibrils of the fabric due to the large size of the molecules [15]. Thus too much high molecular weight PEG would leave white crusts on the surface of the fabric [16]. Thus present study focused on using a combination of both high as well as low molecular weight PEG for STF formation. An optimized amount of high molecular weight PEG as an additive in combination with low molecular weight PEG, as a liquid medium for STF, can result in a more effective STF.

Table 8.1 Properties of different molecular weight PEG

S.No.	PEG molecular weight	Average number of repeating oxyethylene units (n)	Hydroxyl value (mg KOH/gm)	Appearance at 25^{0}C
1	200	3	500-550	Viscous colorless liquid
2	4600	105	25-32	Granular powder
3	6000	152	16-22	Clear white flakes
4	10000	181	9-12	White flakes

In the present work, we systematically study viscoelastic properties by investigating the effect of concentration, temperature and molecular weight of PEG as additives in a common reference STF of 20% fumed silica in PEG200 under both steady and dynamic rheology.

8.2 Processing

To synthesize the STF containing different additives firstly, a certain amount of PEG (molecular weight 4600, 6000 and 10000) was added to PEG200 and heated to 65^{0}C to properly disperse the flakes of high molecular weights PEG and then sonicated by ultrasonication probe (6 mm dia, 40% power) sonicator for 2 min . Secondly, fumed silica was added with simultaneous sonication for 15 min. Typically adding only moderate amounts of high molecular weight PEG results in significant increase in system viscosity resulting in difficulty in the dispersion of particles. Therefore the concentration for high molecular weight PEG is taken up to only 4.76 weight % or 5 phr (parts per hundred of resin/STF) which was also found to be the maximum concentration of high molecular weight PEG as an additive without dramatically decreasing flowability of the STF. Additionally, for a comparison between shear thickening and Newtonian behavior suspensions containing 3 phr (2.91weight %) of high molecular weight PEG in PEG200 without silica particles were also prepared.

8.3 Results and discussion

8.3.1 Characterization

Transmission Electron Microscopy (TEM) was used to characterize the morphology of STF samples. From TEM image of 20% fumed silica STF without any additive (Figure 8.1a), it can be seen that the fractal fumed silica particles are nearly spherical in shape but the average size is increased to about 12 nm as compared to the 11 nm size of the fumed silica particles. The increase in size confirms the formation of a solvation layer of 1 nm thickness by PEG200 around the fumed silica particles. This has also been reported in several studies [17]. Interestingly, on addition of 3 phr PEG4600, the solvation layer further increases and particle size increase to about 15 nm as shown in Figure 8.1b.

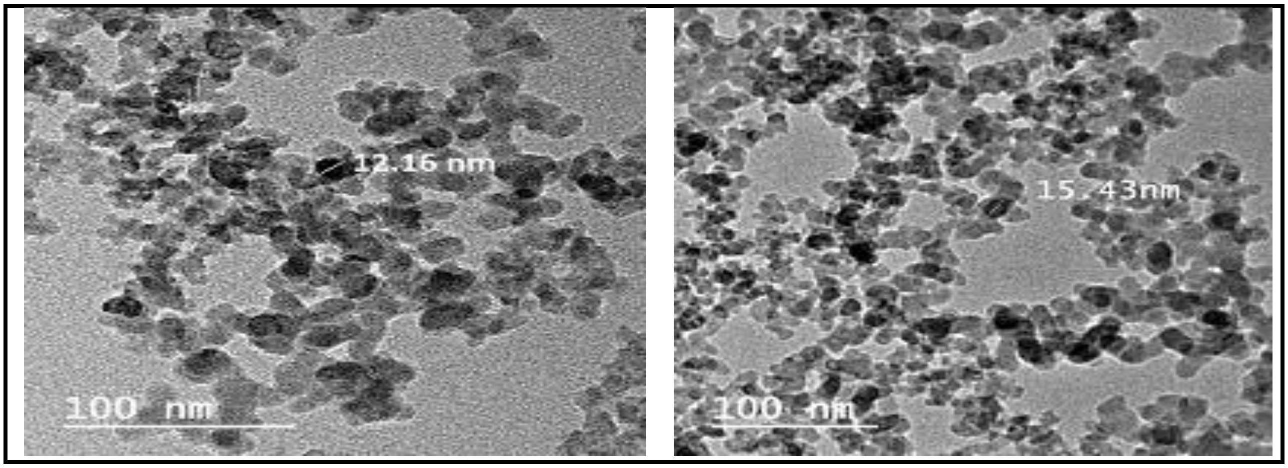


Figure 8.1 TEM images of 20% fumed silica STF a) without any additive and b) with 3 phr PEG4600

8.3.2 Rheology

8.3.2.1Steady-state rheology

Rheological analysis has been carried out at three different concentrations of high molecular weight PEG4600, 6000 and 10000 as 1, 3 and 5 phr in 20% fumed-PEG200 STF. High molecular weight PEG will provide solvation force and steric-hindrance that will give an effective repulsive barrier for the colloidal aggregation, rendering solution stability at low shear and zero shear conditions. The 1 phr is the lowest concentration and 5 phr is the highest concentration studied as more than 5 phr concentration causes shear thinning and also leads to a flocculated or gel state. Figure 8.2 shows the steady-state rheology of 20% fumed silica-PEG STF along with different molecular weights PEG added as additives and profiles of 3 phr concentration of PEGs added to PEG200 without fumed silica at 25^{0}C. All samples consisting of fumed silica particles shows shear thickening behavior after critical strain. The suspensions without fumed silica particles, however, approach Newtonian behavior without much change in viscosity with high shear rates. Compared to STF without additives, the suspension with additives show high shear thickening properties.

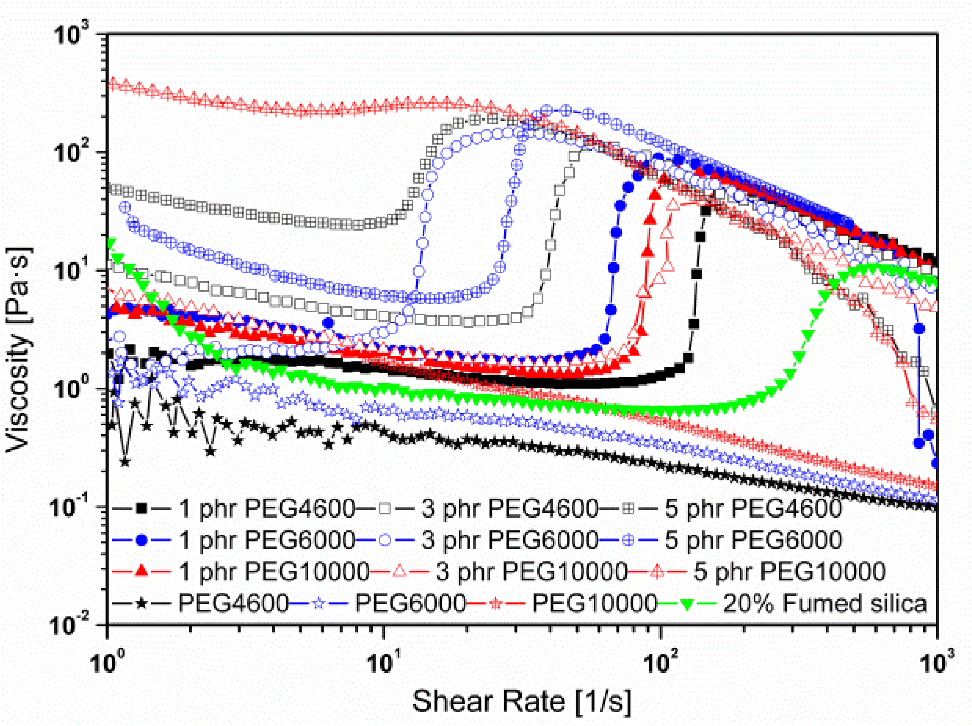
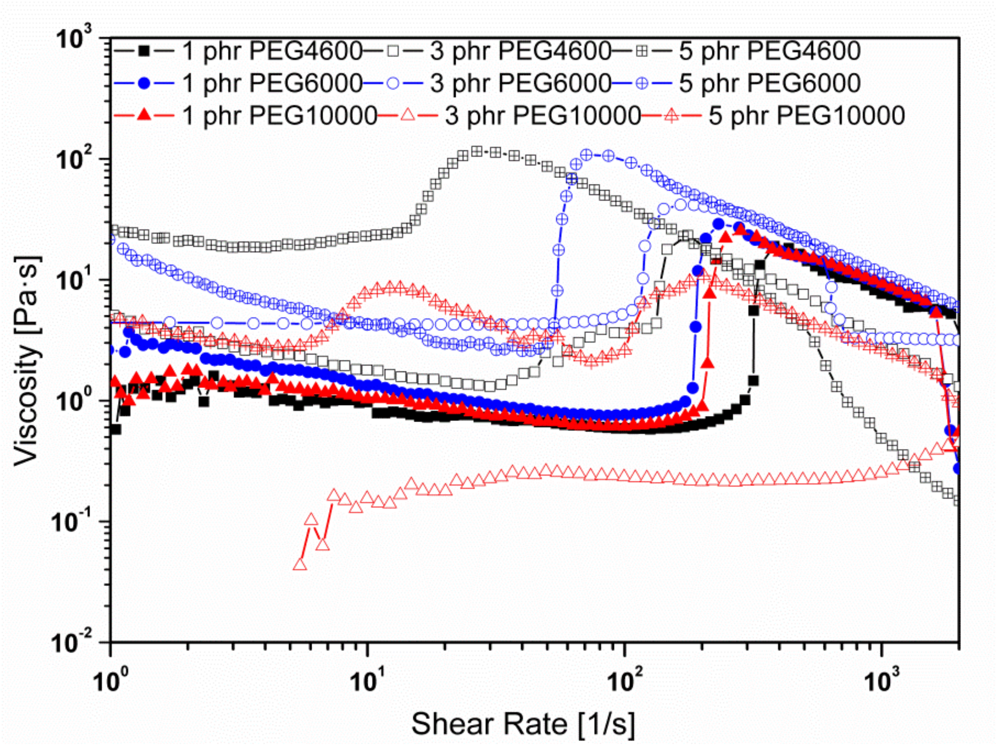
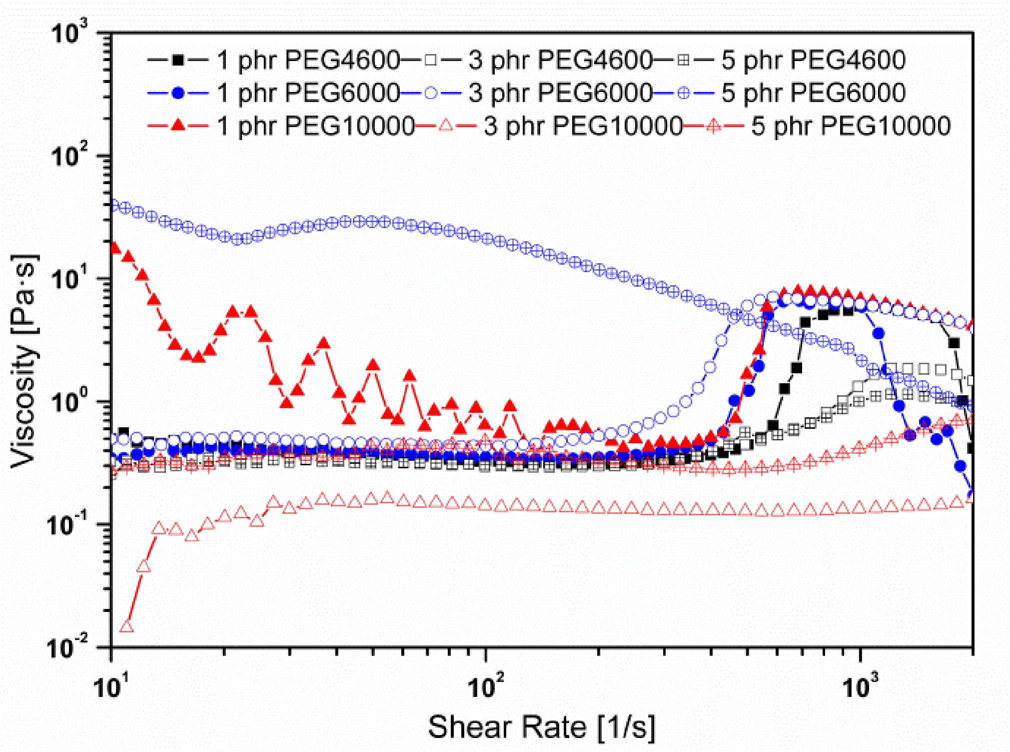


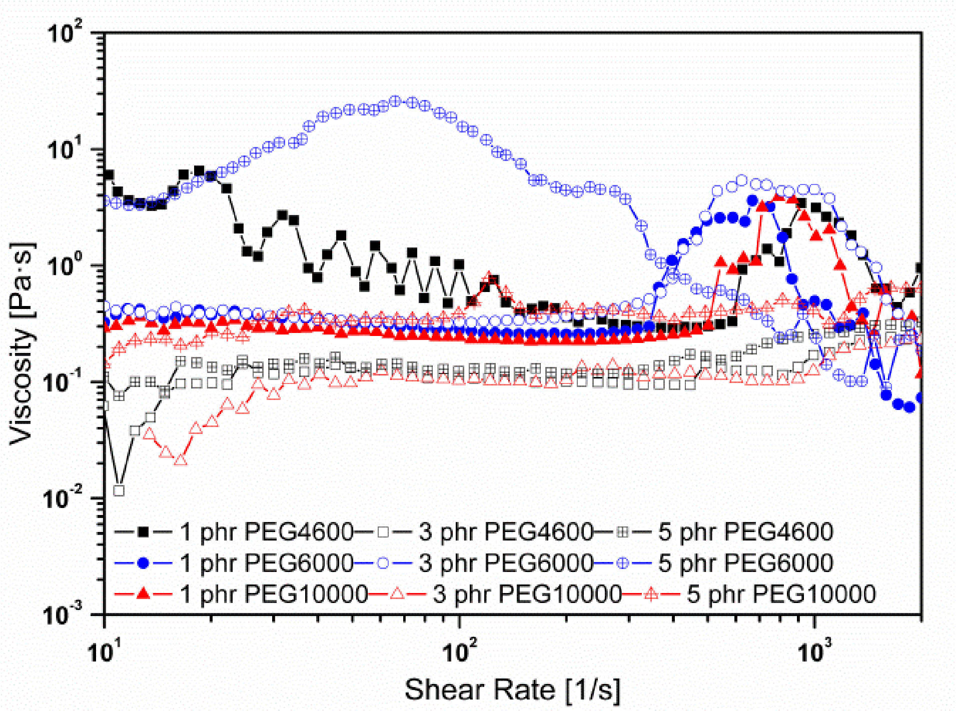
Figure 8.2 Steady-state rheology of 20% fumed silica-PEG STF along with different molecular weight PEGs added as additives to 20% fumed silica-PEG STF and profiles of 3 phr concentration to only PEG200 at 25^{0}C.


1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000
Viscosity [Pa·s]
Shear Rate [1/s]
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{0}
10^{1}
10^{2}
10^{3}

(a)

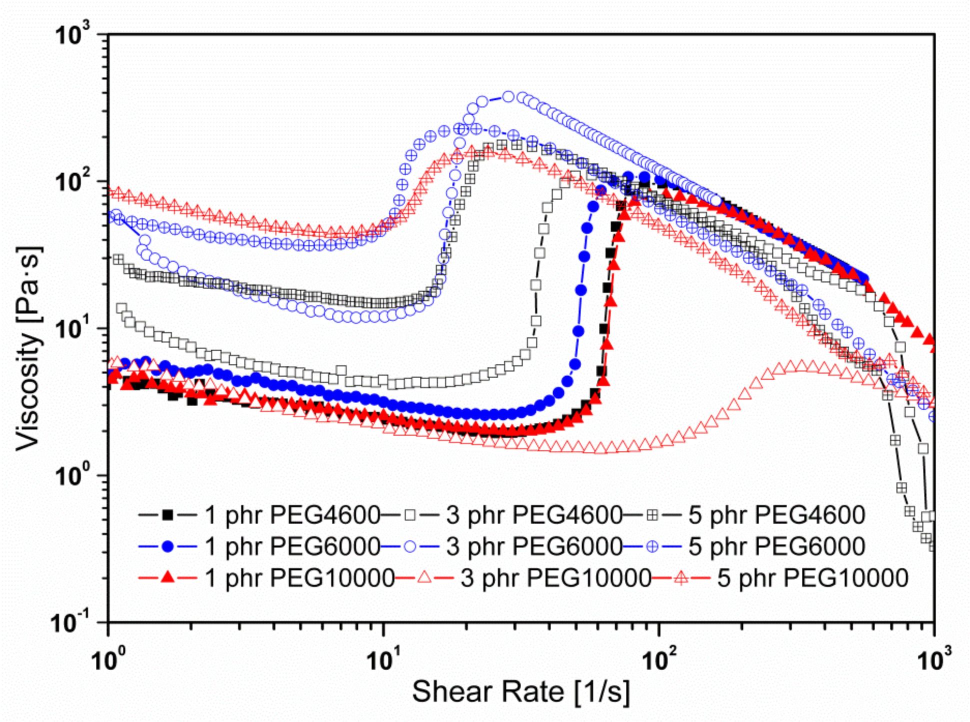

1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000
Viscosity [Pa·s]
Shear Rate [1/s]
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{1}
10^{2}
10^{3}

(b)

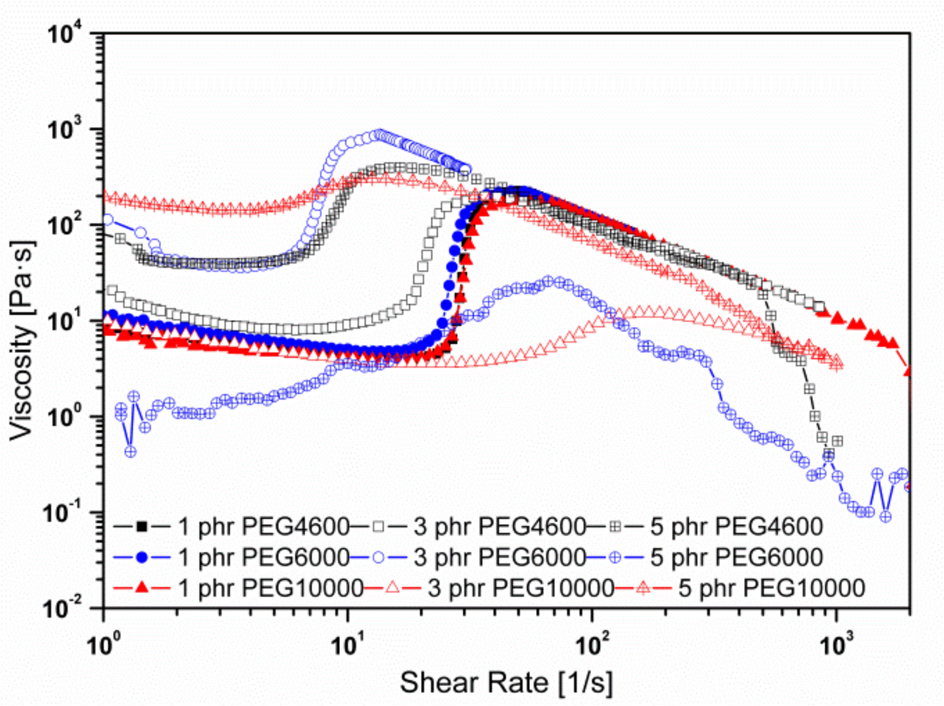


(c)

Figure 8.3 Steady-state rheology for different molecular weight PEGs added as additives to 20% fumed silica-PEG200 STF at a) 35^0C, b) 45^0C and c) 55^0C



(a)



(b)

Figure 8.4 Steady-state rheology for different molecular weight PEGs added as additives to 20% fumed silica-PEG200 STF at a) 15^0C and b) 5^0C

As concentration and molecular weight of PEG increases shear thickening increases i.e. critical shear rate values decreases and critical viscosity values increases. It has been noted that the decrease in critical shear rate with increase in concentration is not much but increase in viscosity is very significant compared to the results reported in Chapter 5 of study with clay particles as additives [1]. At 1 phr concentration, PEG6000 shows maximum value of critical viscosity (about 100 Pa.s) compared to 1 phr PEG4600 (50 Pa.s) and 1 phr PEG10000 (75 Pa.s) but as concentration increases to 3 and 5 phr, critical viscosity values of PEG4600 and 6000 become comparable whereas critical viscosity values of PEG 10000 decreases a lot. 5 phr PEG6000 as additive show maximum critical viscosity followed by 5 phr PEG4600 and their corresponding 3 phr samples respectively. At low shear rates, network structures are broken down and the suspension behaves as a visco-elastic fluid. When the long loops of polymers extending from silica particles come in to contact with the surface of bare silica-particles, the bonds of polymer chains are formed between particles. Generally, more than one polymer molecules are required to bridge large particles, whereas fumed silica particles are much smaller than the coils of high molecular weight PEG thus, only a small segment (low concentration) of a long polymer chain is required. Moreover, one PEG molecule can extend through many bridges by intrachain bridging i.e. one polymer chain adsorbs on to two or more particles to bind them together also one molecule of PEG can extend through several particles [18-19]. Thus it is critical to take only a small concentration as additives i.e <5 phr only.

The rheology of 5 phr PEG10000 does not show shear thickening behavior. Also, it is noted that 1 phr PEG10000 show high shear thickening than 3 phr PEG10000. As molecular weight increases branching increases, cross-linking increases, hydrodynamic radius increases but hydrogen bonding with the particles decreases. Considering that PEGs of very high molecular weight has very less number of terminal hydroxyl, hydrogen bonds between fumed silica and PEG molecules are less and interactions are relatively weak, so fumed silica particles get away from the constraint of molecules easily and participate in the formation of flocculated structure or gel resulting in high viscosity at very low shear rates only and shear thinning at high shear rates. This is similar to the situation observed in weakly hydrogen bonding liquids including end capped oligoethers and higher n-alkanols [15]. At higher concentration the remaining fluid that has not bounded with the silanol surface groups acts as lubrication between fumed silica particles, increase interparticle distance, reducing hydrodynamic interactions requiring larger external forces to overcome this separation distance. Additionally, the larger polymer chain possibly can result in entanglements with other polymer chains within STF, resulting in increased viscosity at low shear rates and difficulty to rearrange themselves under low to medium shear rates. Thus, STF rheology for 5 phr PEG10000 as an additive result in an increase in critical shear rate and a decrease in shear thickening region. Hence high molecular weight PEGs up to only a certain concentration can increase the shear thickening behavior

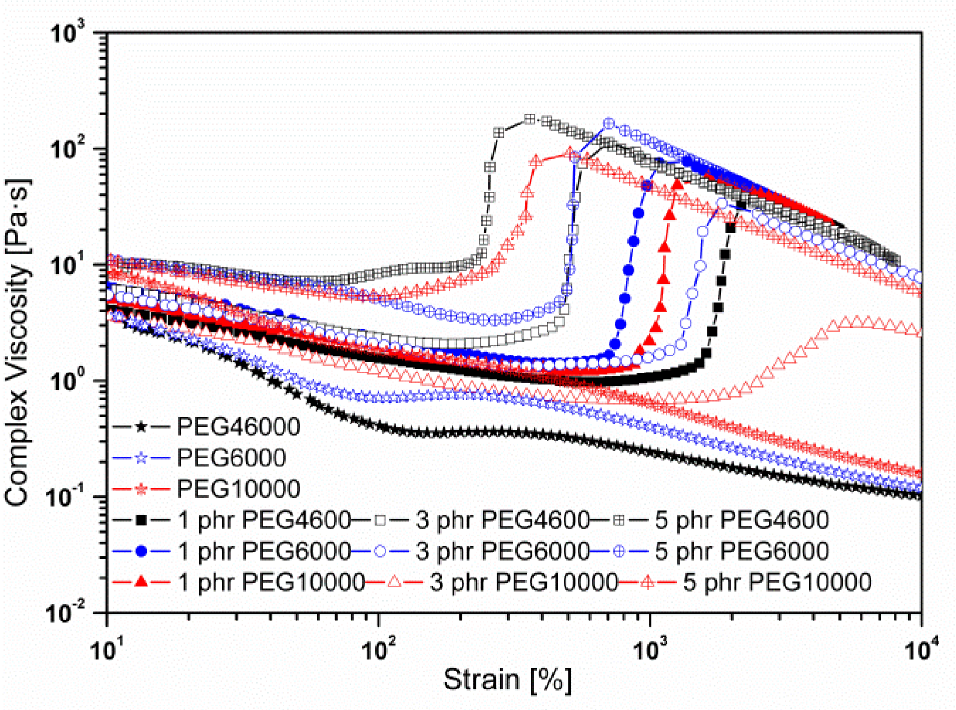
For studying the effect of temperature, the steady-state rheology was also done at different temperatures. All steady-state results are also tabulated in Table 8.2. From 25^{0}C (Figure 8.2) to 35^{0}C (Figure 8.3a) viscosity of 5 phr PEG4600 decreases from 250 to 150 Pa.s and that of 5 phr PEG6000 from 300 to 140 Pa.s. For all other samples including PEG10000, the critical viscosity at 35^{0}C remains under 30 Pa.s. At high temperatures of 45^{0}C and 55^{0}C (Figures 8.3b and 8.3c) only PEG6000 shows appreciable shear thickening. When temperature increases to 45^{0}C, the samples show critical viscosity less than 15 Pa.s with 5 phr PEG6000 showing maximum and PEG10000 showing very negligible shear thickening. At 55^{0}C (Figure 8.3c), 5 phr PEG6000 shows some random rheological behavior due to initial flocculation and gel formation and for all other compositions, the critical viscosity is below 6 Pa.s due to the reason that at high temperature the hydrogen bondings decrease. At lower temperatures of 15^{0}C (Figure 8.4a) and 5^{0}C (Figure 8.4b), maximum shear thickening is shown by 3 phr PEG6000 followed by 5 phr PEG4600. It is interesting to note that at 5^{0}C, 5 phr PEG6000 shows random behavior similar to the behavior shown at a very high temperature of 55^{0}C and 3 phr PEG10000 shows lowest shear thickening at both 15^{0}C and 5^{0}C. Additionally, another compelling observation is that at low temperatures 5 phr PEG10000 also shows appreciable shear thickening. This behavior is the result of the increase of hydrogen bonding as temperature decrease which contributes to the hydrocluster formation. The critical shear rate is greater than 10 s^{-1} at all temperatures except at 5^{0}C. The steady-state rheological results show that a high concentration of high molecular weight PEGs did not show high shear thickening at low and high temperatures. Consequently, PEG6000 shows maximum shear thickening at both low and high temperatures but up to 3 phr concentration only.

Table 8.2 Steady-state rheological parameters of different concentrations of high molecular weight PEGs when added to the base composition of 20% fumed silica-PEG200 STF, at different temperatures

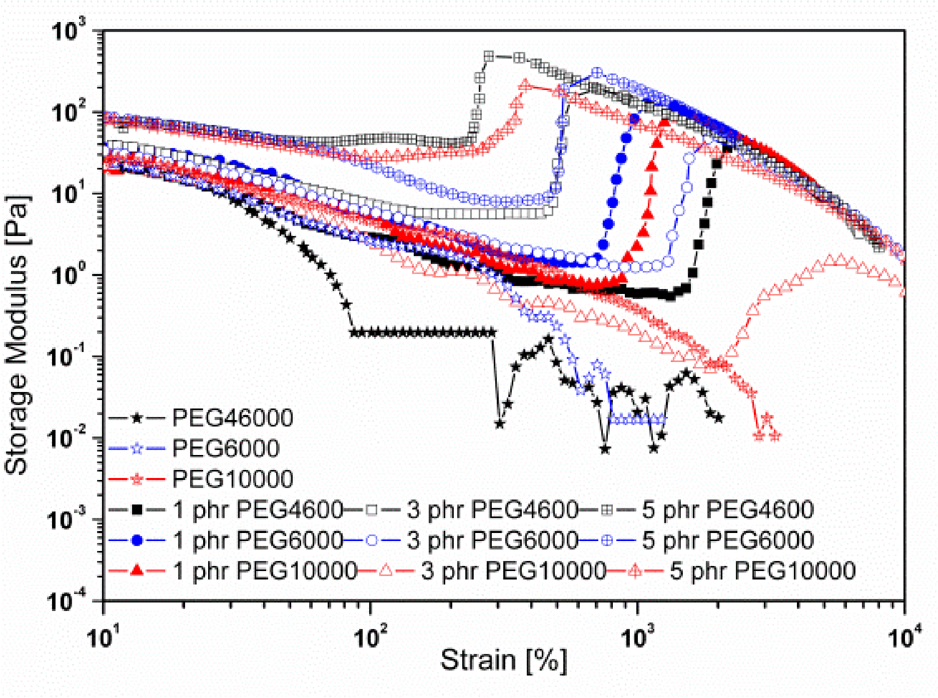
Compo-sition (phr)	PEG molecular weight (additive)	**Critical viscosity (Pa.s) at different temperatures (^{0}C)**						**Critical shear rate (s^{-1}) at different temperatures (^{0}C)**					
		5	**15**	**25**	**35**	**45**	**55**	**5**	**15**	**25**	**35**	**45**	**55**
1	4600	220	100	50	25	6	3	25	50	100	200	400	600
	6000	250	150	100	40	10	4	20	40	50	140	300	300
	10000	200	100	75	45	15	3	20	50	55	150	300	500
3	4600	300	150	140	30	3	0.4	10	30	30	40	400	900
	6000	100	500	150	60	10	6	7	20	10	70	200	300
	10000	15	8	50	Not observed	Not observed	0.2	30	100	55	Not observed	Not observed	900
5	4600	500	250	250	150	1.5	0.6	7	20	10	15	400	600
	6000	30	300	300	140	Not observed	Not observed	10	10	20	40	Not observed	Not observed
	10000	400	250	Not observed	20	0.6	Not observed	7	10	Not observed	70	300	Not observed

8.3.2.2 Dynamic-state rheology

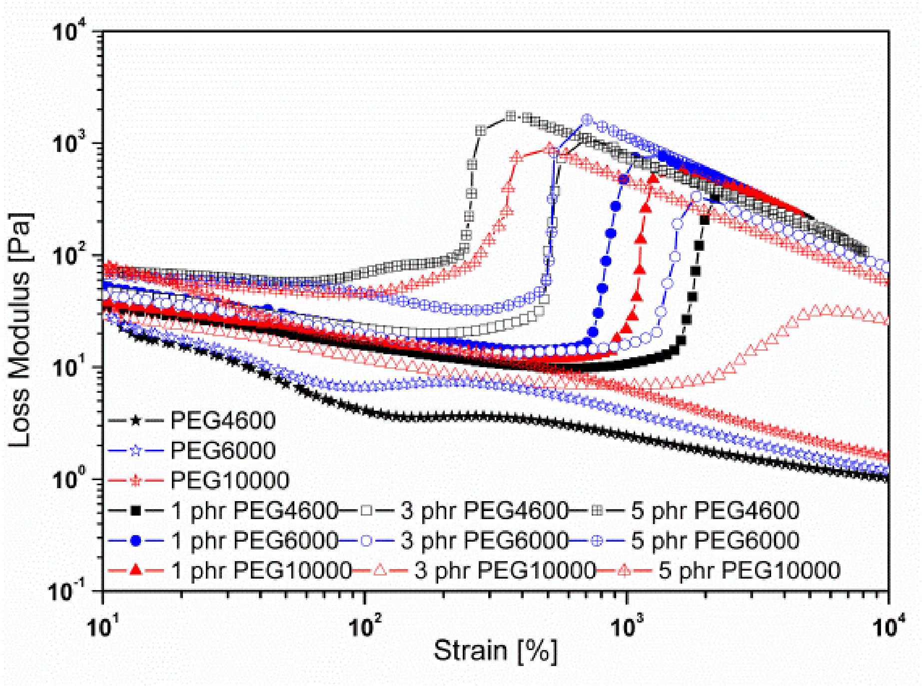
The strain percent was linearly swept from 1% to 10000% and the frequencies selected were 10, 30, 50 and 70 rad/s. Figure 8.5a shows that complex viscosity profiles of 3 phr concentration of PEGs in PEG200 without fumed silica are similar to those at steady-state rheology i.e. approaching Newtonian behavior without strain thickening. For all other samples, initially at low strains linear relationship is obtained between dynamic parameters and strain up to critical strain. During the linear range it is noted that for low concentrations of 1 and 3 phr, loss modulus is large than storage modulus however for 5 phr of all PEGs the difference between the loss modulus and storage modulus is very small which indicates that high molecular weight PEGs have more elastic properties which increase as concentration increases. After critical strain, nonlinearity increases and both moduli increase with loss modulus values very high than the storage modulus. Table 8.3 displays the dynamic state rheological results after critical strain for all samples at all frequencies studied. In dynamic state strain sweep at 10 rad/s, PEG6000 similar to steady-state rheology showed the highest value of critical complex viscosity and values increases as concentration increases to 5 phr (250 Pa.s). However, at a high constant value of frequencies, PEG4600 and PEG6000 show similar behavior. As compared to steady state viscosity there is a slight decrease for 5 phr of PEG6000 and there is a large decrease in critical values of complex viscosity for PEG10000. The slight decrease in values of complex viscosities with an increase in frequency is may be due to rapid formation and rupture of hydroclusters in the dynamic sweep which restrict the formation of clusters of large size. However, as frequency increase critical strain values decrease a lot as displayed in Table 8.3. It has been observed that as frequency increases from 10 to 30 rad/s there is a slight decrease in complex viscosity and a slight increase in loss modulus but storage modulus increases by two times.


Complex Viscosity [Pa·s]
Strain [%]
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{1}
10^{2}
10^{3}
10^{4}
PEG46000
PEG6000
PEG10000
1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000

(a)

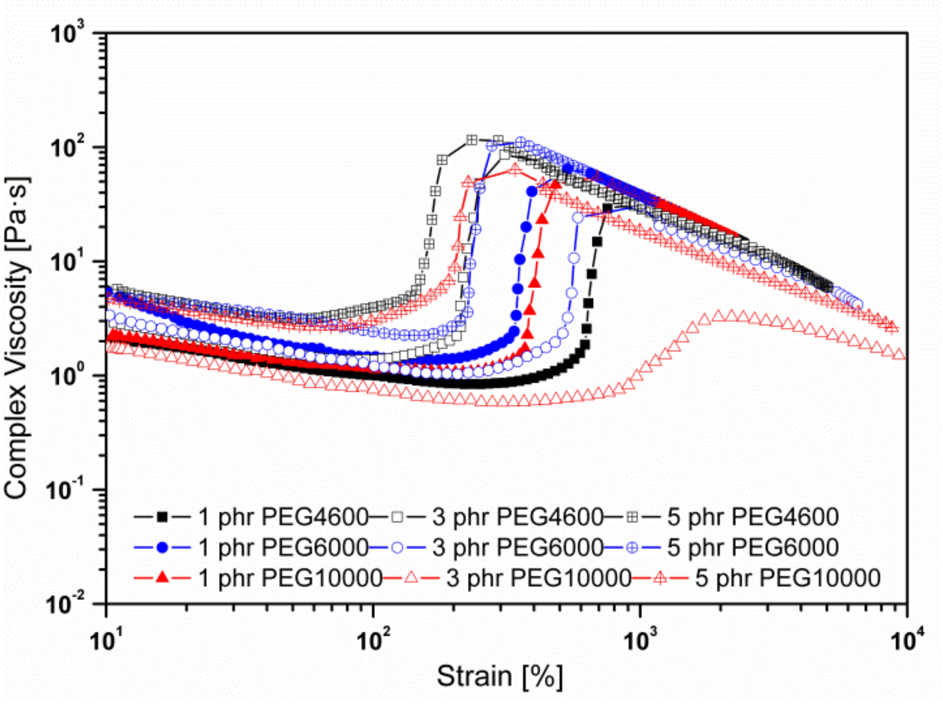

Storage Modulus [Pa]
Strain [%]
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{1}
10^{2}
10^{3}
10^{4}
PEG46000
PEG6000
PEG10000
1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000

(b)

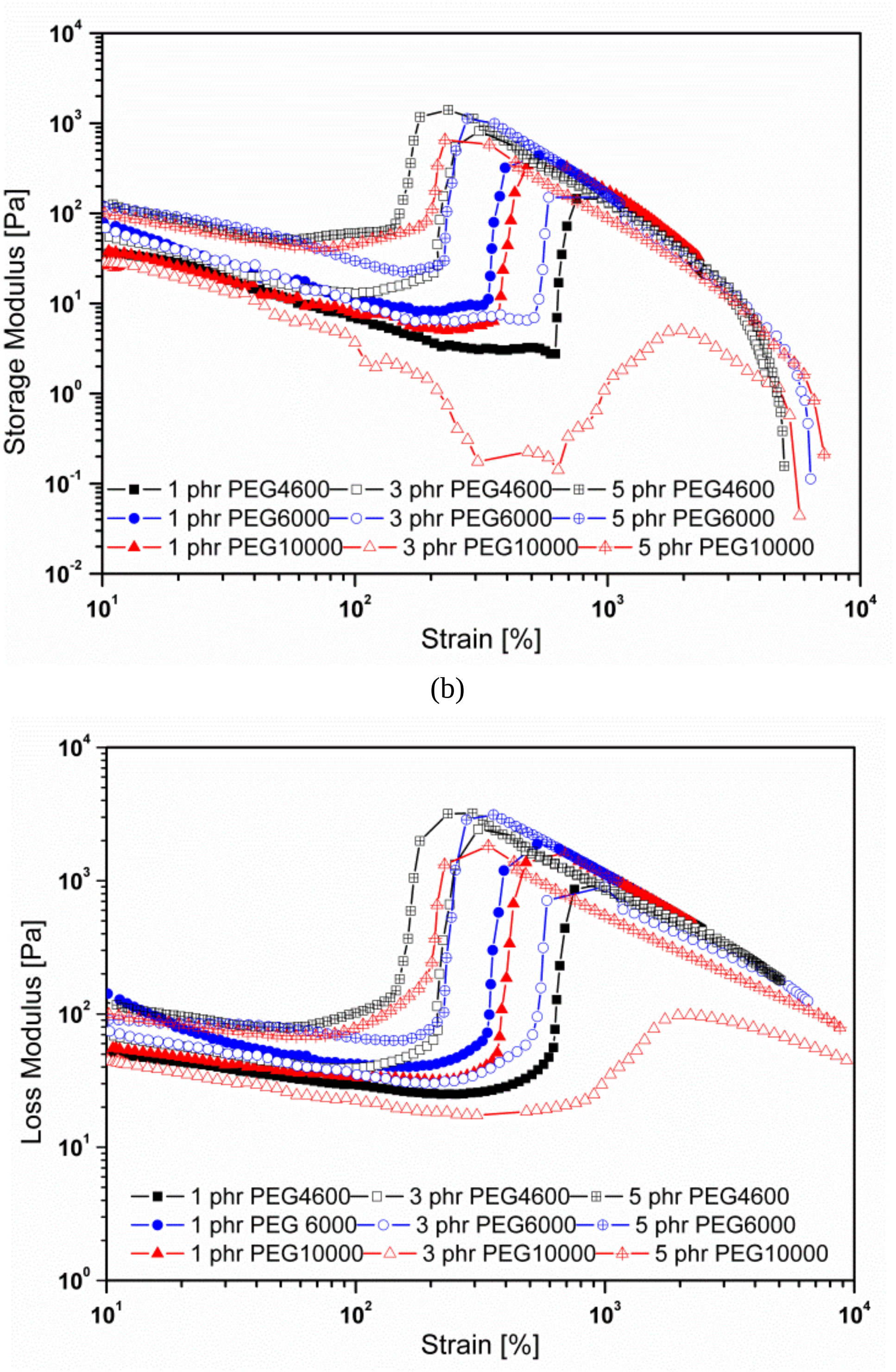


(c)

Figure 8.5 a) Complex viscosity b) storage modulus and c) loss modulus of different molecular weight PEGs added as additives to 20% fumed silica-PEG STF and profiles of 3 phr concentration to PEG200 only at 25^0C in strain sweep at 10 rad/s



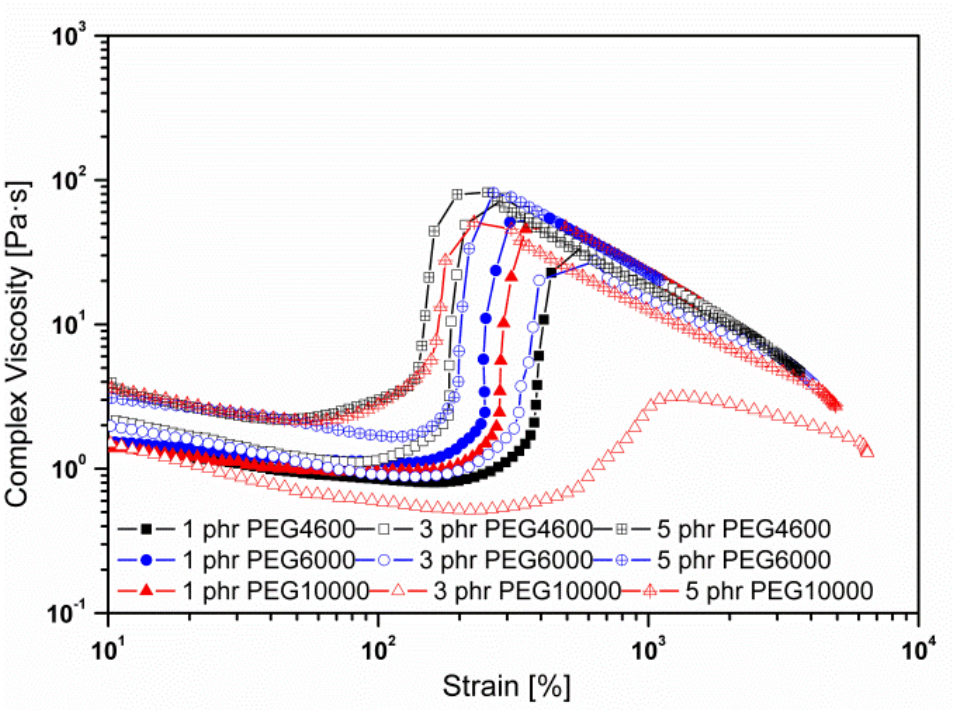
(a)



(b)

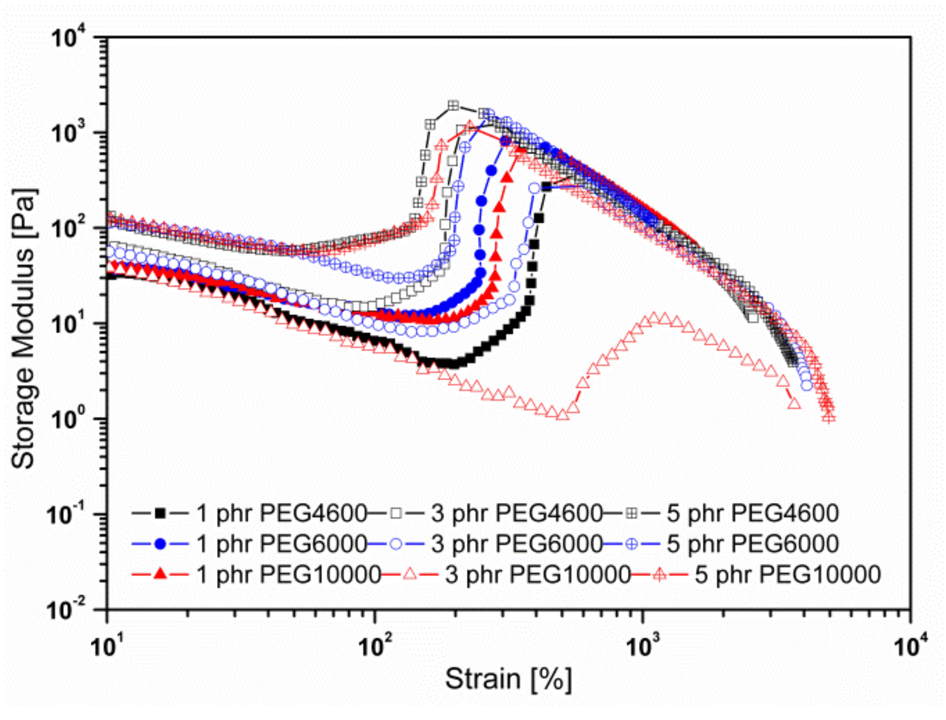
(c)

Figure 8.6 a) Complex viscosity and b) storage modulus and c) loss modulus of different molecular weight PEGs added as additives to 20% fumed silica-PEG STF and profiles of 3 phr concentration to PEG200 only at 25^{0}C in strain sweep at 30 rad/s



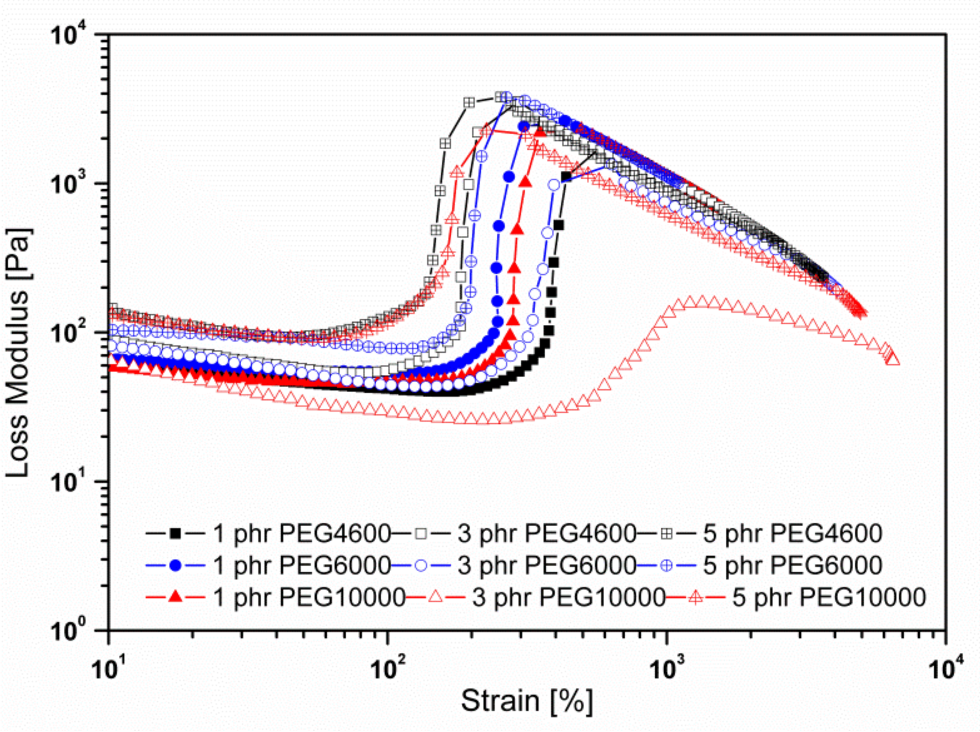
Complex Viscosity [Pa·s]
10^3
10^2
10^1
10^0
10^{-1}
10^1
10^2
10^3
10^4
Strain [%]
1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000

(a)



Storage Modulus [Pa]
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
10^3
10^4
Strain [%]
1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000

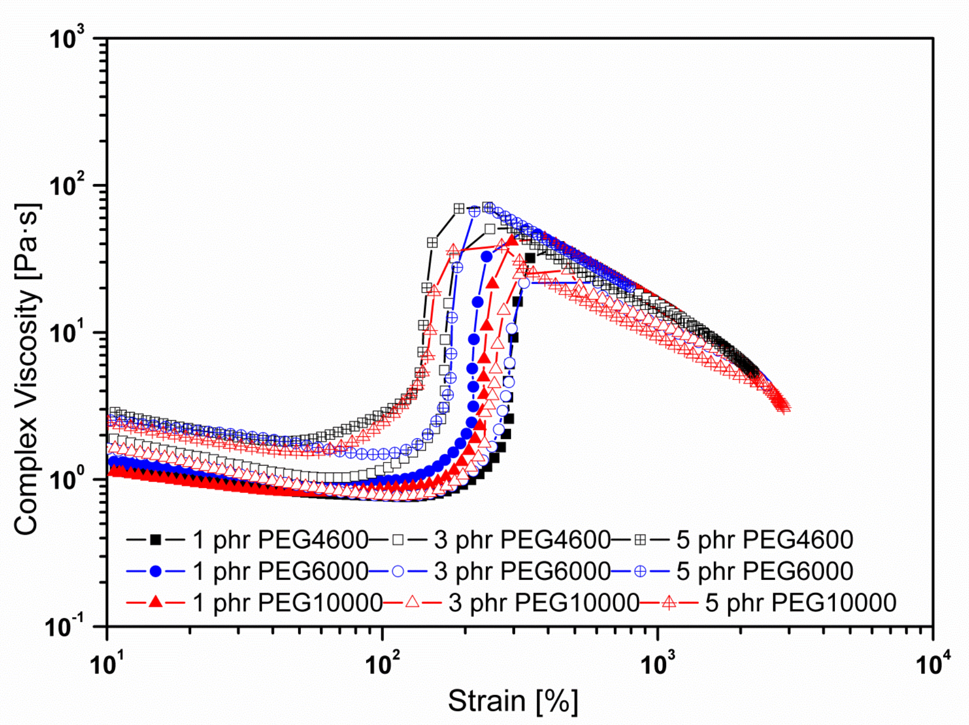
(b)



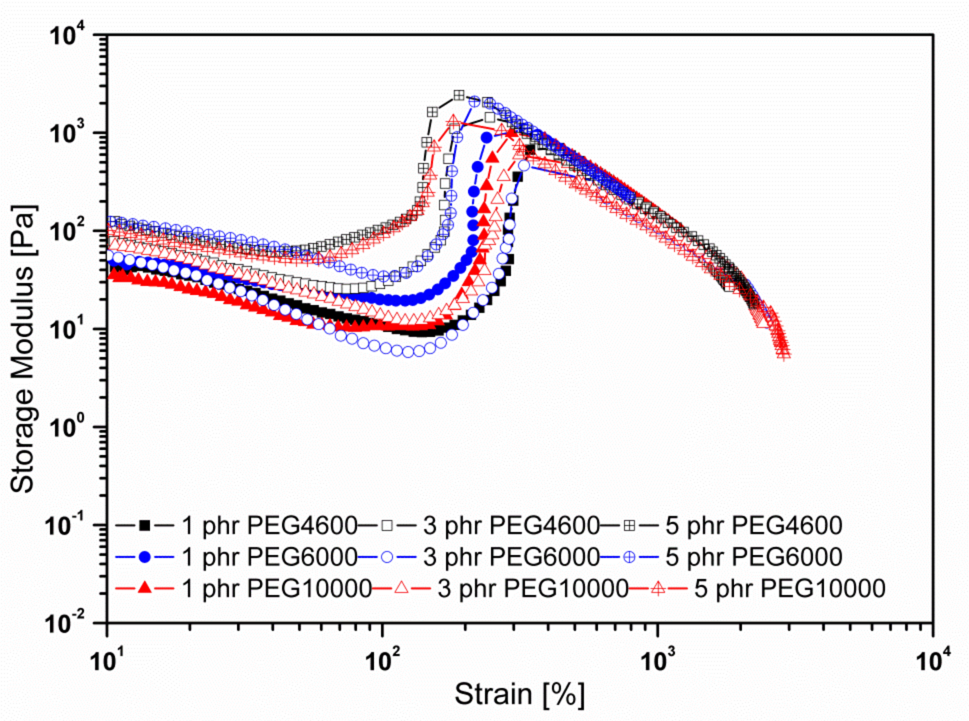
(c)

Figure 8.7 a) Complex viscosity and b) storage modulus and c) loss modulus of different molecular weight PEGs added as additives to 20% fumed silica-PEG STF and profiles of 3 phr concentration to PEG200 only at 25^{0}C in strain sweep at 50 rad/s

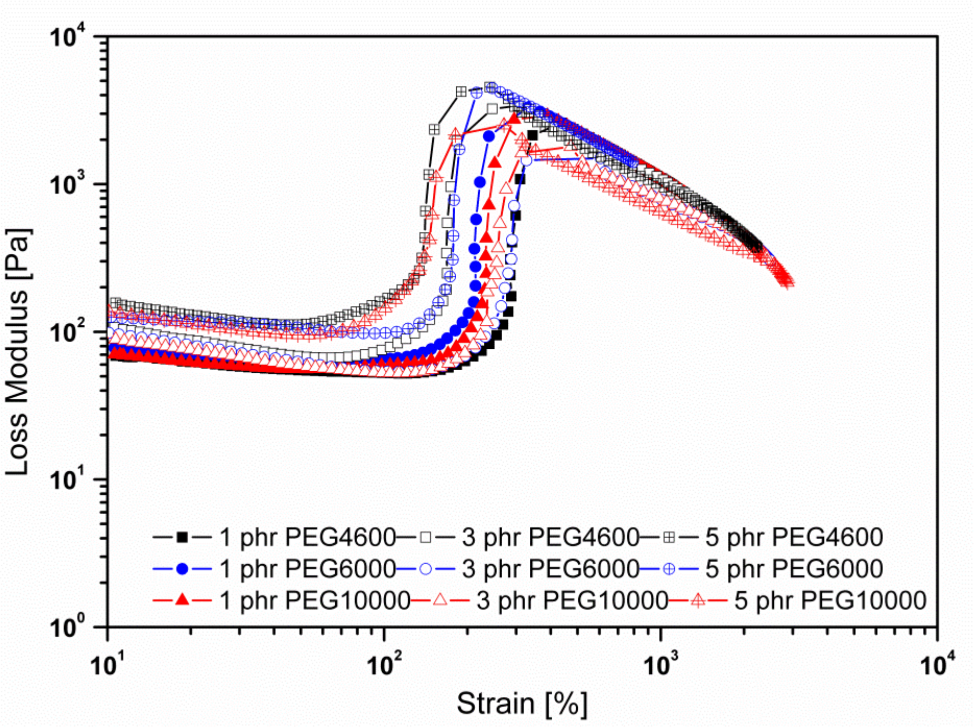
However, at 50 rad/s (Figure 8.7b), only a slight increase in storage modulus is seen which shows that storage modulus becomes almost constant at higher frequencies. Negligible change in both moduli, as well as complex viscosity, is observed at 70 rad/s (Figure 8.8). Additionally, the range of critical strain and critical viscosity of all samples decreases as frequency increases i.e. maximum and minimum values of critical viscosities of samples at 10 rad/s is 250 and 50 Pa.s whereas at 70 rad/s it is 90 and 30 Pa.s. The similar trend of order is followed by loss and storage moduli. It is interesting to note that, 1 phr concentration for both PEG6000 and 10000 show more shear thickening than 3 phr concentration. Results show that as frequency increases both moduli increases contributing to decreasing critical strain values and an overall increase in strain thickening behavior. Thus from dynamic strain sweep, it can be concluded that a high concentration of high molecular weight PEGs increases the dynamic parameters and again PEG6000 is the transition molecular weight.


Complex Viscosity [Pa·s]
Strain [%]
10^3
10^2
10^1
10^0
10^-1
10^1
10^2
10^3
10^4
1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000

(a)


Storage Modulus [Pa]
Strain [%]
10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
10^1
10^2
10^3
10^4
1 phr PEG4600
3 phr PEG4600
5 phr PEG4600
1 phr PEG6000
3 phr PEG6000
5 phr PEG6000
1 phr PEG10000
3 phr PEG10000
5 phr PEG10000

(b)



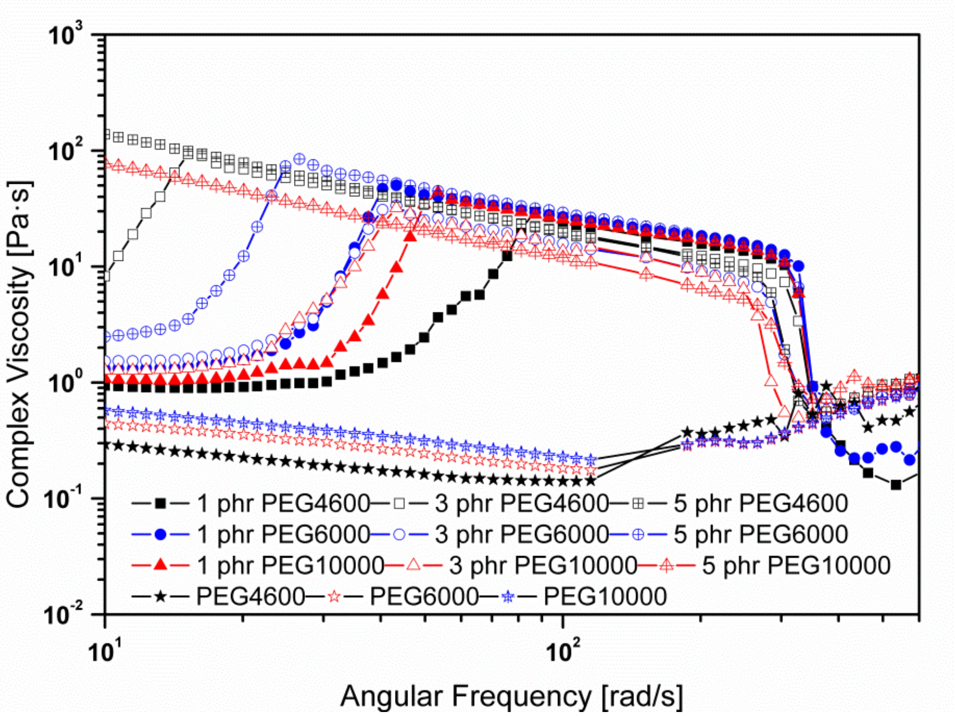
(c)

Figure 8.8 a) Complex viscosity and b) storage modulus and c) loss modulus of different molecular weight PEGs added as additives to 20% fumed silica-PEG STF in strain sweep at 70 rad/s

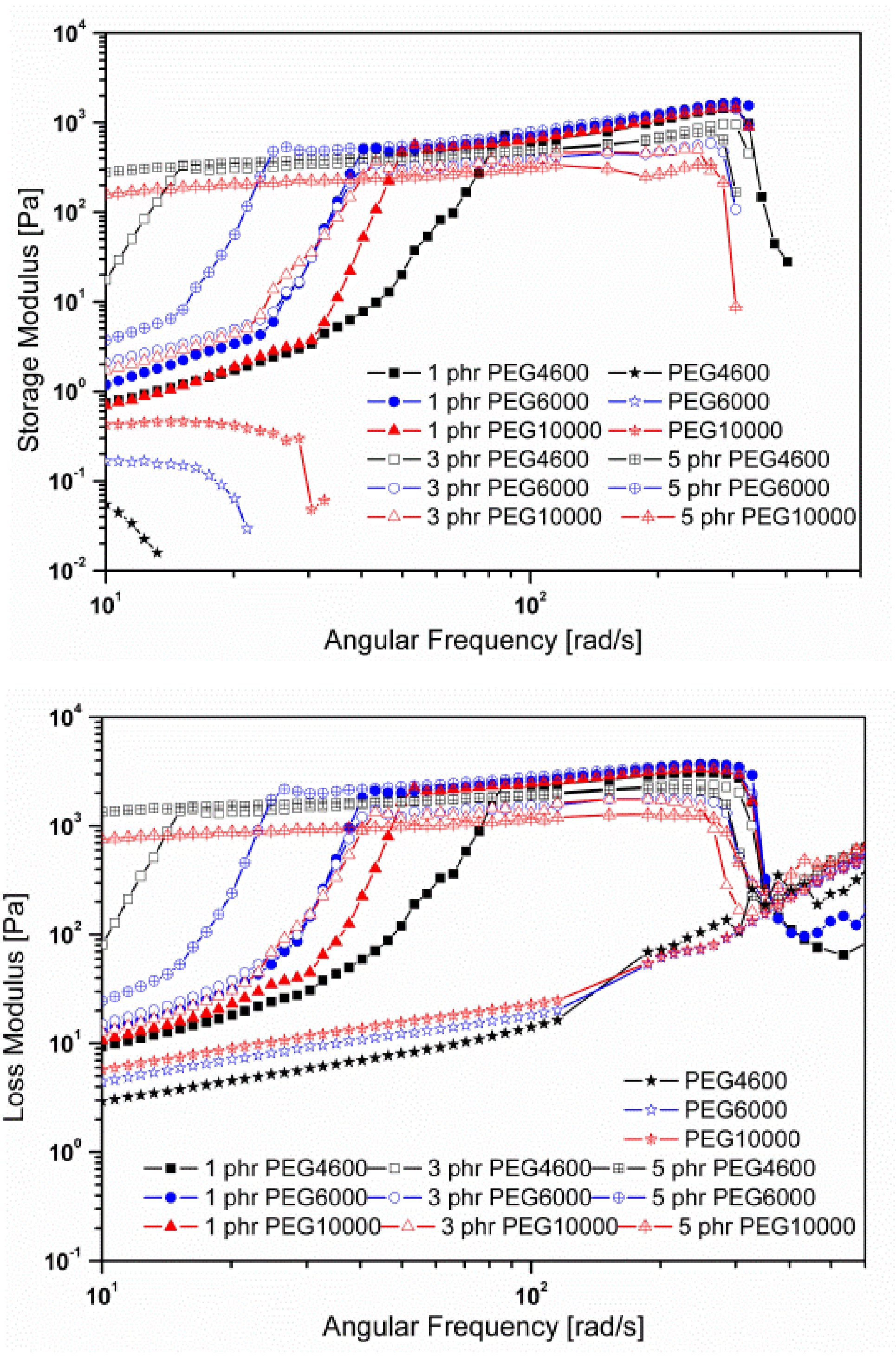
Table 8.3 Dynamic-state strain sweep rheological results at frequencies of 10, 30, 50 and 70 rad/s

S.No.	Frequency (rad s^{-1})	Strain thickening range (%)	Critical Complex viscosity range η_c^* (Pa.s)	Storage Modulus range G′ (Pa)	Loss Modulus range G″ (Pa)	Compositions exhibiting the highest critical viscosity
1		200-400	100-250	500-250	1000-2000	5 phr 6000
2		700-1150	50-100	100-40	800-350	1 phr 4600
3	10	2000	5	15	30	3 phr 10000
4		100-300	80-150	500-1500	3000-2000	5 phr 4600
5		400-600	40-60	200-400	800-1500	1 phr 4600
6	30	900	5	50	100	3 phr 10000
7		100-190	80-90	1100-2000	3500-4000	5 phr 4600
8		210-350	40-55	300-900	1500-3000	1 phr 6000
9	50	500	3.5	15	150	3 phr 10000
10		110-150	60-80	1500-2500	2500-5500	5 phr 4600
11		150	45	1500	2500	5 phr 10000
12	70	190-210	30-50	600-1000	3000-2000	1 phr 10000
13		250	25	550	1500-1800	3 phr 6000

Next, all samples were studied in frequency sweep to understand the impact of frequency on shear thickening behavior. Frequency sweeps were done at constant strains of 500% and 900%



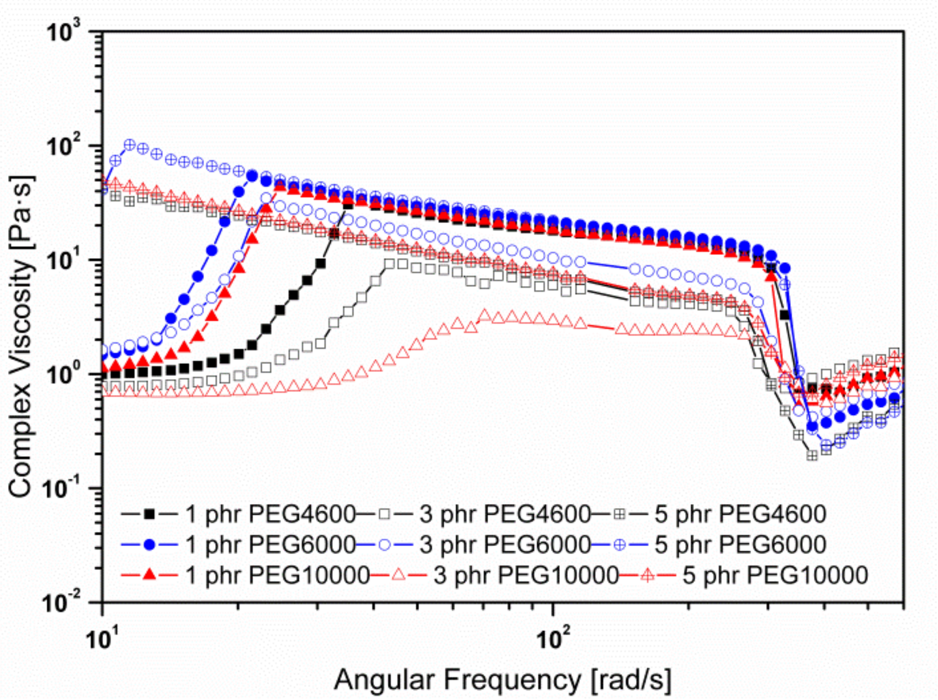
(a)



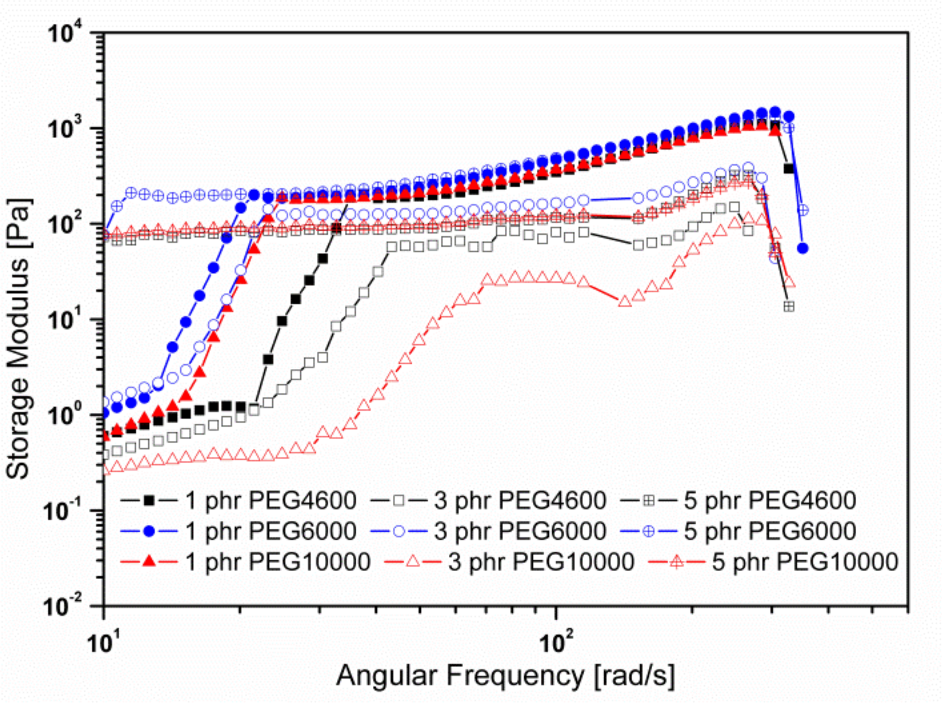
(b)

Figure 8.9 a) Complex viscosity and b) Storage modulus and c) loss modulus of different molecular weight PEGs added as additives to 20% fumed silica-PEG STF and profiles of 3 phr concentration to PEG200 only at 25^{0}C in angular frequency sweep at 500%

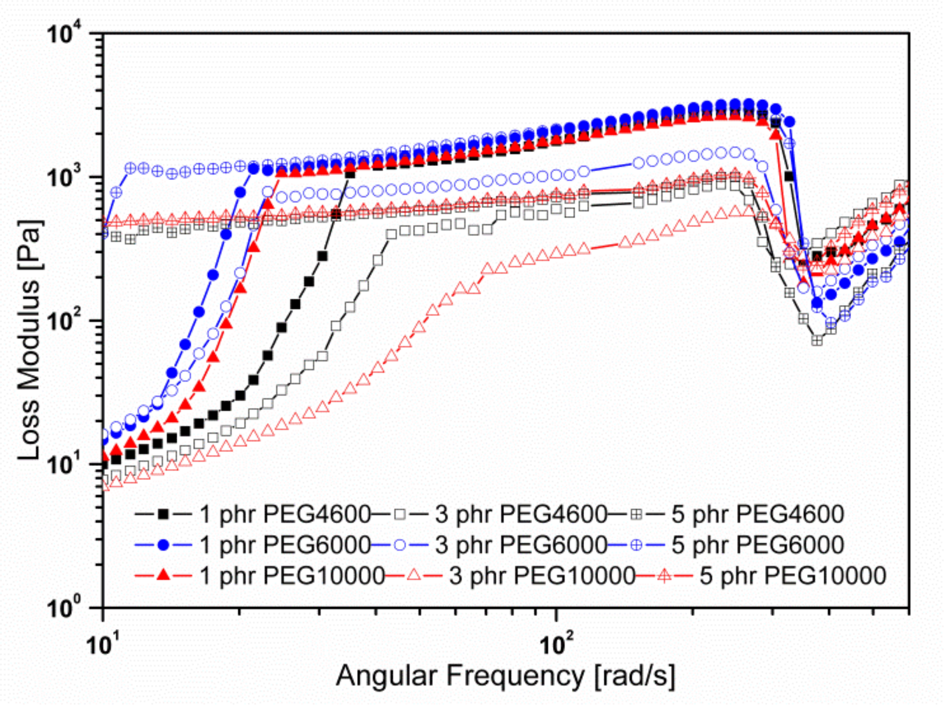
Figures 8.9 and 8.10 shows the frequency sweep profiles of complex viscosity, loss modulus and the storage modulus at a constant strain of 500% and 900% strain respectively. Table 8.4 displays the results of frequency sweep at both strains. Here also 5 phr PEG6000 as additive show maximum value of critical viscosity. It is noted that as frequency increases, all parameters increases sharply for all samples containing additives until a plateau region is reached except samples of 5 phr concentration of PEG4600 and 10000 which already show increased values of parameters. Rheology of suspensions containing only PEGs shows almost constant complex viscosity and loss modulus values up to around 100 rad/s followed by a random increase, however, storage modulus decreases a lot showing negligible elasticity of these suspensions.



(a)



(b)



(c)

Figure 8.10 a) Complex viscosity b) Storage modulus and c) loss modulus of different molecular weight PEGs added as additives to 20% fumed silica-PEG STF in angular frequency sweep at 900%

Frequency sweeps show that only up to certain critical frequency (about 70 rad/s), shear thickening properties increases with increase in frequency followed by a linear plateau region which is slightly decreasing for complex viscosity profile (Figure 8.10a) and slightly increasing for the profile of both the moduli (Figures 8.10b and 8.10c). These results are analogous with the results obtained in strain sweep. Frequency sweep at 900% quantitatively shows similar behavior to that at 500% with plateau region starting at slightly lower frequencies value than those in 500% which is again correlative with amplitude sweep tests that, at higher strains, low frequency is required for shear thickening and vice-versa. For 500% and 900% strain, increase in values of both the moduli in plateau region is almost the same with loss modulus greater than storage modulus with a more scattered profile at 900% strain.

8.3.3 Stability

Stability of the STF with respect to time is a very important issue. Figure 8.11 demonstrates the effect of storage time on the morphology of STF containing high molecular weight PEG4600 as an additive. As shown in Figure 8.11a STF is liquid-like and at this stage, all rheological studies were done. After a week, soft gel (Figure 8.11b) like structure is observed which on storing for another about three weeks turns in to a hard gel (Figure 8.11c).

Both these forms show considerable shear thinning behavior. However, it is important to note that on ultrasonication, this gel behavior is reverted to liquid-like behavior with same shear thickening properties as seen in freshly prepared samples. However, there is a 30-50% decrease in overall viscosity values as shown in Figure 8.12. This decrease is more in samples with high molecular weight PEGs at high concentration due to possible gelling of PEGs leading to aggregation of particles. These comments about the STF stability confirm that in both synthesis and manufacture, the prepared STF should not be stored for more than one to two weeks.

Table 8.4 Frequency sweep at different strains

Strain (%)	Critical frequency (rad s^{-1})	Critical complex viscosity η_c^* (Pa.s)	Storage modulus G′ (Pa)	Loss modulus G″ (Pa)	Compositions
500	Not observed	Not observed	800	2000	5 phr 4600
			300	1000	5 phr 1000
	15	100	2000	4000	5 phr 6000
		90	1000	2500	3 phr 4600
	20	60	2000	4000	1 phr 6000
		35	600	2000	3 phr 10000, 3 phr 6000
	30	50	2000	3500	1 phr 10000
		20	2000	3000	1 phr 4600
900	Not observed	100	1000	2500	5 phr 6000
		Not observed	300	900	5 phr 10000
		45	300	900	5 phr 4600
	15	60	1500	3000	1 phr 6000
		40	400	1500	3 phr 6000
	20	50	1000	2000	1 phr 10000
	30	30	1000	2500	1 phr 4600
		9	150	800	3 phr 4600
		4	100	600	3 phr 10000

Figure 8.11 STF with 3 phr PEG4600 a) freshly prepared sample (viscous liquid) b) after a week (soft gel) and c) after a month (hard gel)

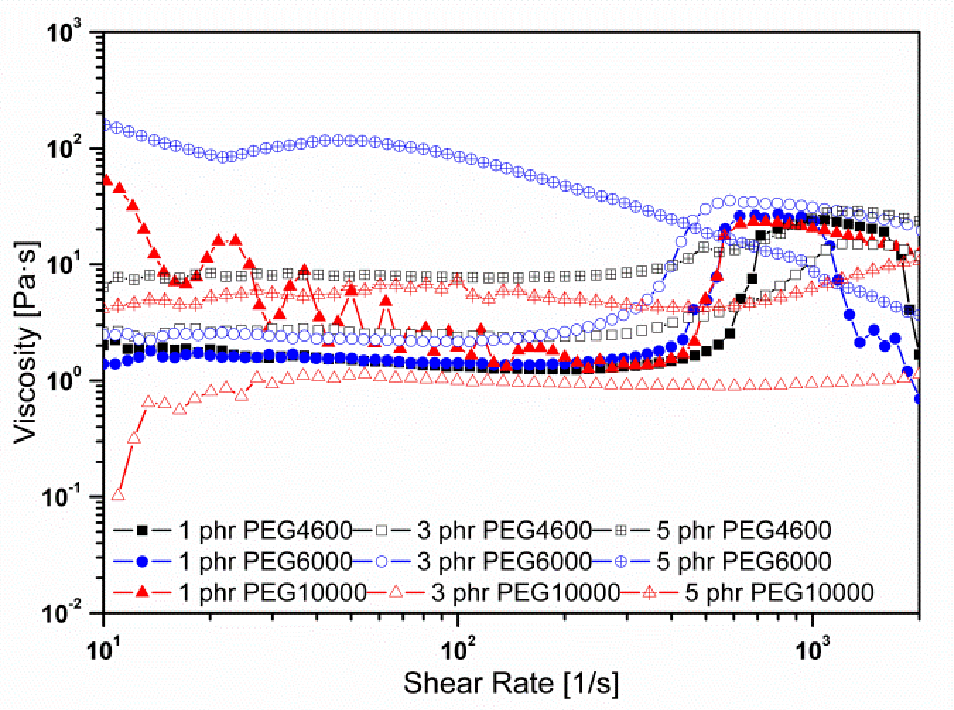


Figure 8.12 Steady-state rheology for different molecular weight PEGs added as additives to 20% fumed silica-PEG STF after a month of storage.

8.4 Conclusion

The STF comprising of fumed silica (hydrophilic) particles in PEG200 with different molecular weight PEGs as additives demonstrates enhanced shear thickening behavior. The 5 phr PEG6000 exhibits an excellent shear thickening behavior with appreciable critical shear rate and high critical viscosity. As molecular weight further increases to 10000, shear thickening phenomena decrease with increase in concentration due to less hydrogen bonding with silica particles. Along with concentration of PEG as an additive, temperature also greatly affects the shear thickening behavior. Shear thickening decreases a lot at high temperatures. However, shear thickening for all samples increases a great deal at low temperatures especially more for high concentration and high molecular weight PEG as the additive. Interestingly, PEG10000 at 5phr shows noticeable shear thickening at lower temperatures. Thus, it can be inferred that the liquid medium significantly influences the rheological properties of the STF when using the same concentration of fumed silica in STF.

The dynamics of these systems are thus strongly influenced by the ability of the polymer to bridge fumed silica particles which is also consistent with the explanation given by Antosik et al [5]. The difference between steady-state and dynamic-state viscosity increases as the molecular weight of PEG increases. Storage modulus is more sensitive to the frequency and increases much more than the loss modulus, but become constant at higher frequencies (about 50 rad/s). High molecular weight PEG, due to high entanglements, show more elastic nature at low frequencies. The critical values of shear rate obtained for the samples studied are about 100 s^{-1} and range of critical strain values is 100 to 1000% with critical values of frequency varying from 10 to 50 rad/s. With an increase in PEG molecular weight, the increase in shear thickening properties and easy processing shows an optimum behavior for PEG6000. As a result, PEG with high molecular weight under some limitations can be used as additives for increasing shear thickening behavior due to their high cross-linked molecular structure and capability of forming bridges. Addition of high molecular weight PEG as an additive to fumed silica PEG STF can improve the ST properties that can translate to increased performance in various applications.

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Chapter 9 Effect of addition of silicone oil on the rheology of fumed silica and polyethylene glycol shear thickening suspension

The viscosity of the liquid dispersant of shear thickening fluid (STF) should ideally lead to an increase in shear thickening properties at an appreciable shear rate, high elasticity, and at the same time should also prevent the flocculation of particles on storage by allowing uniform dispersion of nanoparticles. In the present study, different silicone oils of varying viscosity were used in the STF of 11nm fumed silica in PEG200, replacing the base dispersant (PEG) in different concentrations. The high viscosity silicone oils have been used as a branched substrate for silica particles to form cross-links resulting in the hydro-clusters formation and provide improved elastic and viscous behavior compared to simple fumed silica-PEG STF. The effect of addition of silicone oil on the propertries of reference PEG STF, were then studied in terms of steady-state and dynamic-state rheological behavior under a wide range of temperature, shear rate, strain rate, and frequency.

This study is based on: Effect of addition of silicone oil on the rheology of fumed silica and polyethylene glycol shear thickening suspension, Mansi Singh, Sanjeev K Verma, Ipsita Biswas and Rajeev Mehta; Journal of Polymer Engineering, DOI: https://doi.org/10.1515/polyeng-2018-0054 (IF: 0.778)

9.1 Introduction

For customizing the shear thickening properties of STF, different liquid dispersants like viscoelastic fluids consisting of highly branched structures can be used [1]. Conventional viscoelastic fluids i.e. polymer melts or solutions show some elastic properties during deformation provided generally by their long chain molecules [2, 3]. The molecules of polymers do not act alone, however, when particles are dispersed in it, millions of such long chain molecules interloop and entangle resulting in an intramolecular interaction which leads to the formation of large hydro-clusters at high shear rates/strains and thus a large increase in the viscosity of the suspension [4-11]. It is interesting to note that when STF is kept between the layers of the fabrics it leads to a reduced performance under ballistic impact as compared to STF impregnated in the fibrils of the fabric [12]. Therefore, the viscosity of the dispersant medium is limited by the aspect of ability to fill the space in the fibrils of the fabrics. Additionally, in all the materials used as additives for processing of STF a parameter which determines the shear thickening performance of STF is the intermolecular interactions which are influenced by hydroxyl groups, oxygen atoms, crosslinking and branching. Consequently, the choice of materials for processing of STF will depend on a number of factors such as toxicity, compatibility with other materials, physical, chemical, cost, and rheological properties. In the present study, STF systems are made by fumed silica nanoparticles dispersed in PEG-silicone oil. In order to verify an actual effect of silicone oil, STF were processed in which as compared with reference STF some concentration of PEG was replaced by silicone oil. The referential sample was STF of fumed silica in 20% concentration by weight dispersed in PEG200 (Figure 9.1a and b. Specifically, the rheological properties of nano-silica dispersed PEG blended with the various amounts of silicone oil of different viscosities as a dispersant liquid has been rheologically investigated and presented in the steady-state and dynamic-state conditions along with an explanation of intermolecular interactions. Three different viscosities (100, 500 and 1000cst) of silicone oil were used to replace 10 and 15 weight % of PEG200. Accordingly, the performance benefits of silicone oil are reviewed in terms of its structural dependent rheological properties which can help meet new processing and application challenges of STF.

9.2 Processing

Unfortunately, silicone oil is not soluble in PEG and when fumed silica particles are directly added to silicone oil, fumed silica forms clusters and immediately large agglomerations are formed as shown in Figure 9.1c. This behavior is a result of the hydrophobic nature of silicone oil that cannot interact with hydrophilic fumed silica. However, a combination of silicone oil up to a limited concentration, with PEG along with fumed silica particles forms a stable suspension. But for higher concentrations of silicone oil as dispersant i.e. replacing >20% of PEG200, the stability (in properties) decreases. Thus the preparation of STF essentially requires a distinct way of mixing sequences of the constituents. Firstly, some part of fumed silica

is added to PEG followed by probe sonication until the proper dispersion of the particles has taken place. The silicone oil is then added and the suspension is further sonicated. Finally, all of the remaining silica particles are added in small potions by subsequent probe sonication dispersion. After processing, the systems were kept undisturbed for 12h before the rheological experiments, to expel air bubbles trapped during sonication. Thus base dispersant-PEG200 is replaced in two different concentrations by silicone oil i.e. 10% and 15% by weight of the overall dispersant. The lowest concentration of PEG that can be replaced by silicone oil and with an appreciable increase in shear thickening is 10%. Additionally, 15% is the highest concentration for both 500 and 1000cst silicone oil STF. The higher concentration of silicone oil that can be successfully used without causing agglomeration is, limited by the fact that PEG should be able to modify all silicone oil molecules [silicone oil paper]. Moreover, with an increase in the concentration of silicone oil, the flocculation of silica particles is more pronounced as fumed silica particles will not get enough PEG for interaction due to most of the PEG molecules interacting with silicone oil. 15% concentration corresponds to the maximum concentration of both silicone oil of 500cst
as well as 1000cst replacing the PEG in STF.

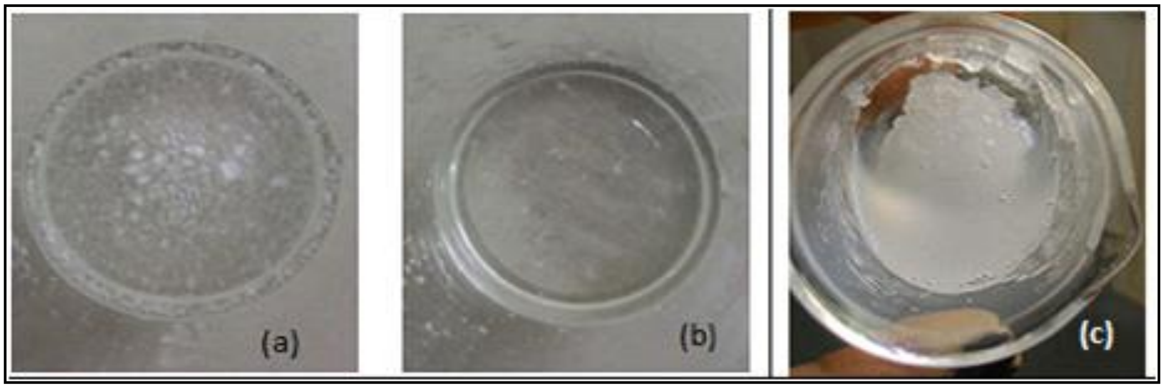


Figure 9.1 Fumed silica dispersed in a) PEG without sonication b) PEG with sonication c) silicone oil with PEG with sonication

9.3 Results and Discussion

Silicone oil has hydrophobic characteristics thereupon the wet ability of hydrophilic fumed silica particles by it is difficult. Thus, modification of silicone oil is required (Figure

9.2a). Thus, silicones can be modified by adding hydrophilic side chains to the branched silicones backbone of inorganic silicon-oxygen (Si-O-Si-O-Si) by polyethers like PEG as shown in Figure 9.2a [13, 14]. Thus, PEG-modified silicone oils will have secondary functionality rendering it hydrophilic [5]. The hydrophilicity of dispersant is thus determined by the ratio of PEG to silicone oil. Additionally, since the viscosity of both silicone oil (about 0.5 and 1 Pa.s) is much more than that of PEG (0.05 Pas), it should increase overall viscosity of the STF. Moreover, both electrostatic and steric forces should also increase with the addition of silicone oil which is important for the stability of the suspensions at zero shear conditions [15].

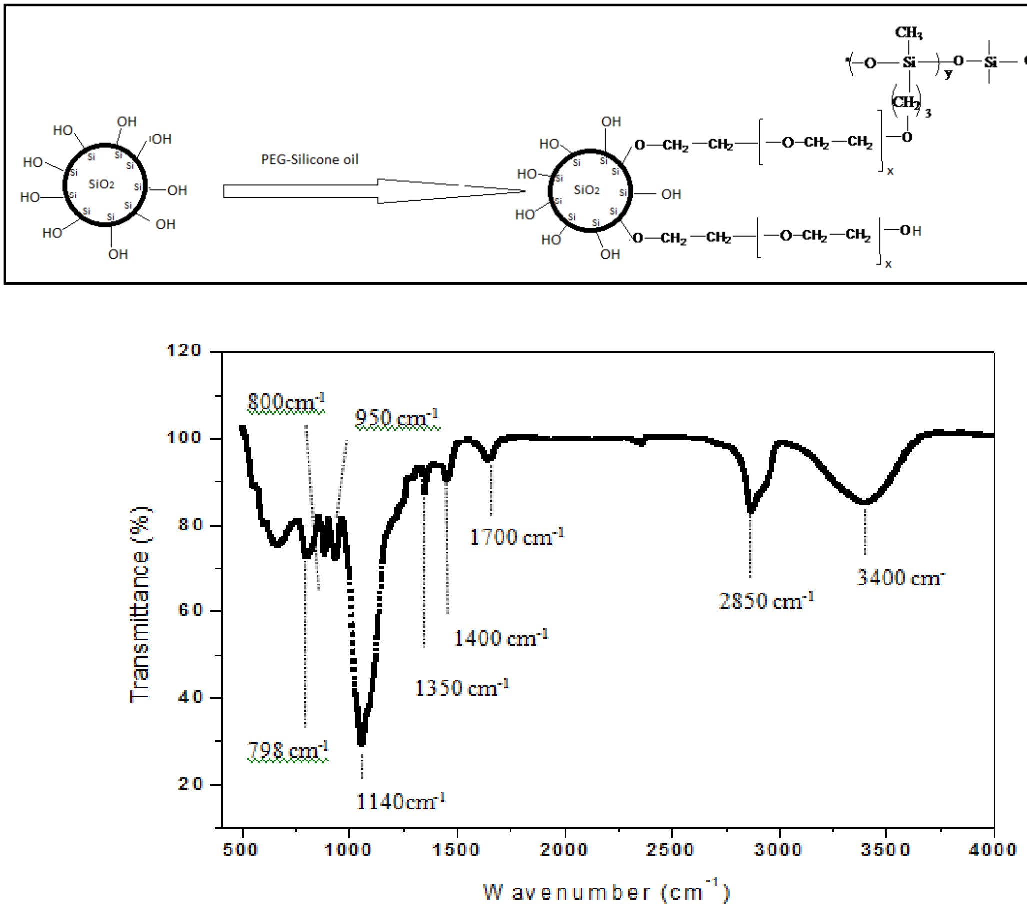


Figure 9.2 a) Adsorption mechanism of silicone oil with PEG on silica nano-particles and b) FTIR spectrum of STF having 20% silicone oil with PEG as the dispersion medium

9.3.1 Characterization

The organic groups in the prepared suspension of 20% PEG replaced by silicone oil of 100cst in STF were identified and verified through the FT-IR spectra [10, 16, 17]. Figure 9.2b illustrates the experimental data along with the FTIR graph. It is observed in Figure 9.2b that the wave number of the largest peak of ether (C-O-C) bonds shifts from 1140 cm^{-1} to 1050 cm^{-1}, which represents the chemical interaction between PEG molecules and silicone oil. The presence of another high-frequency bond of the hydroxyl group at 3300 cm^{-1} which has been shifted from 3400 cm^{-1}, indicates the chemical bonding of PEG molecules with fumed silica particles as well as with silicone oil. All samples of 10%, 15% and 20% of silicone oil with PEG show identical spectra.

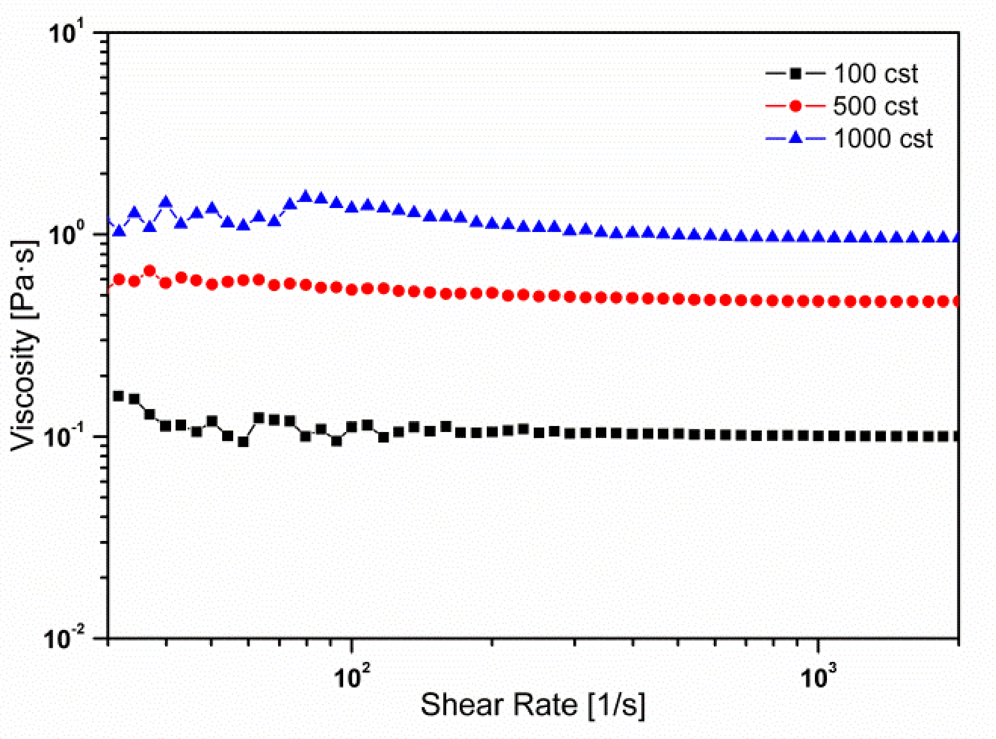
9.3.2 Rheological measurements

9.3.2.1 STF with Silicone oil of viscosity 100cst

Steady-state measurements

Silicone oil shows Newtonian behavior as their viscosity did not change with high shear rate (Figure 9.3a). Many impact sources like high-velocity projectiles occur at relatively high (10^3 s^{-1}) shear rates. However, damping by viscoelastic dampers occurs at low (10^2 s^{-1}) shear rates [18]. Consequently, to describe the viscous properties of the STF samples, steady-state shear tests were done (Figure 9.3b) over a large range of shear rate (0-1000 s^{-1}) for 15% concentration of PEG replaced with different viscosities of silicone oil. It can be seen that as the viscosity of silicone oil increases the critical value of viscosity increases. Figure 9.4 shows steady-state rheology profiles for 100cst silicone oil replacing different concentration of PEG200. Initially, at low (or zero) shear rates viscosity was high due to flocculation of particles, after which it contains three well-defined regions. The first viscosity region is shear thinning region because of the breakage of flocculation by shear and formation of flowing layers of particles followed by a second region where after a critical shear rate shear thickening occurs due to the formation of hydroclusters. It can be seen from Figure 9.4 that the magnitude of the viscosity of different concentrations of silicone oil did not change much at relatively low shear rates until the critical shear rate is achieved. This indicates that the rate of flocculation is not much dependent on the studied concentrations of the silicone oil. At the critical shear rate, the increase in viscosity was abrupt for suspensions containing 15 and 20% of silicone oil (as dlogη / dlogγ values are 0.16 and 0.73 respectively) and the increase was smooth for 0 and 10% silicone (as dlogη / dlogγ values are 0.024 and 0.04 respectively) oil with PEG. As shear rate increases further, the viscosity goes through a maximum value and then again shows an abrupt decrease for 20% and 15% and smooth decrease for 0% and 10% silicone oil compositions. Thus, the third region once again corresponds to the shear thinning region which is due to the deformation of hydroclusters at very high shear rates and after this, no shear thickening was detected. Thus steady-state results manifest that silicone oil due to its more branched structure [19] results in the large hydroclusters compared to those formed in absence of it. 15 and 20% concentration of silicone oil has higher critical viscosity than 0 and 10%. As critical viscosity is inversely related to the critical shear rate, the former occurs at a lower shear rate than the latter.

Even though critical shear rate values decrease it is greater than 50 s^{-1} for all samples. Compared to critical viscosity of 11 Pas for reference sample i.e. 0% of silicone oil, the increase in viscosity with varying add-on percentage of silicone oil varies over a wide range from a minimum of about 13 Pas (for 10 % silicone oil) to a maximum of 45 Pas (for 20% silicone oil) i.e an increase of about 4 times.



(a)

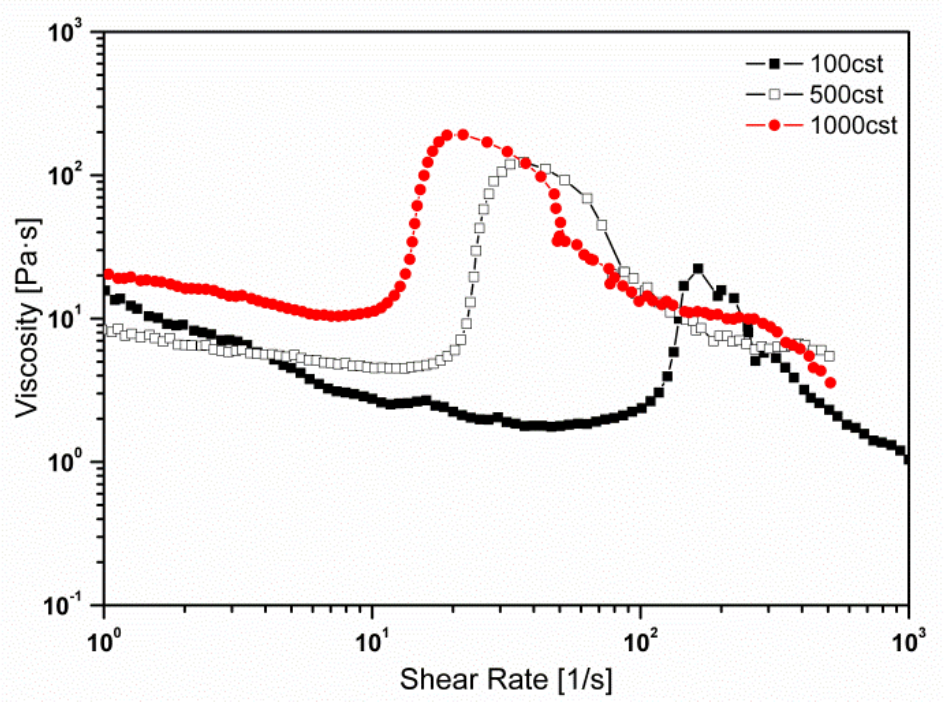


Figure 9.3 Steady-state rheology profiles of a) different viscosities of silicone oil and b) STF of 15% concentration of PEG replaced by silicone oil along with the profile of referential STF

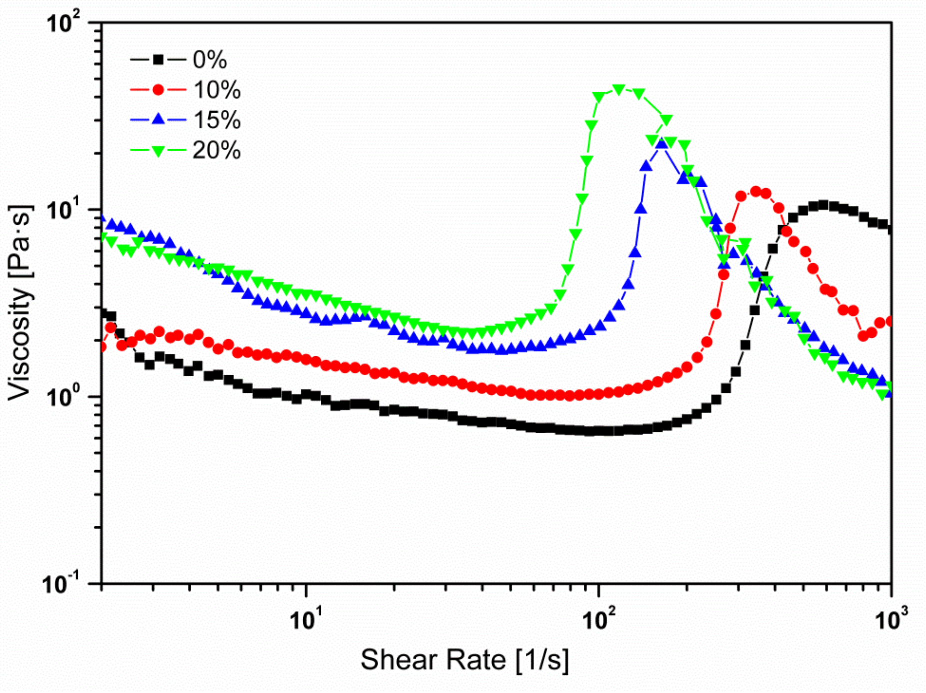
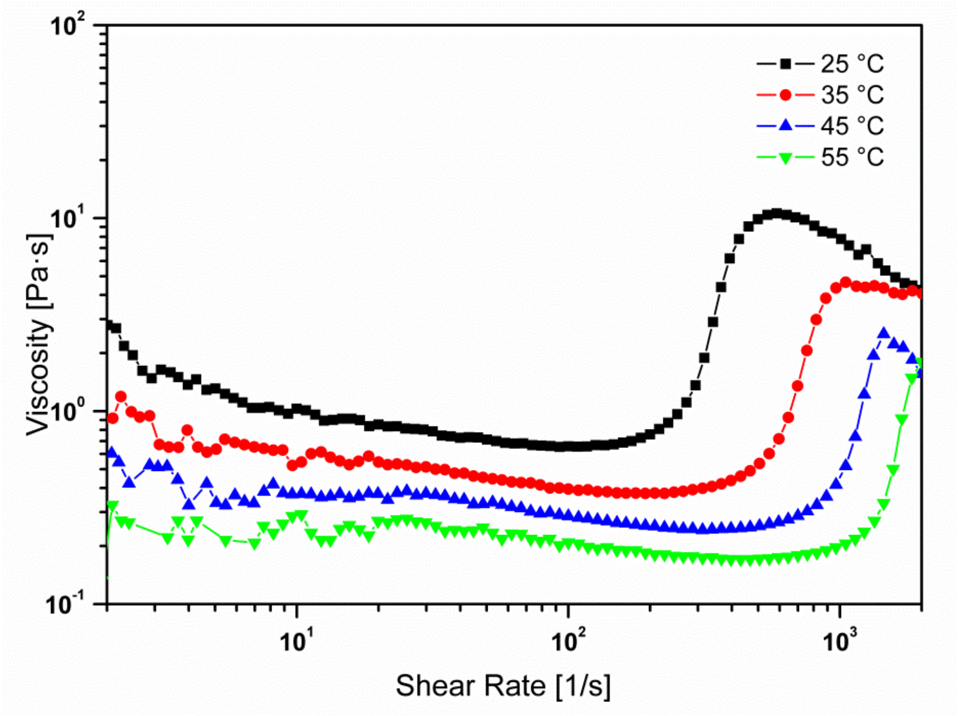
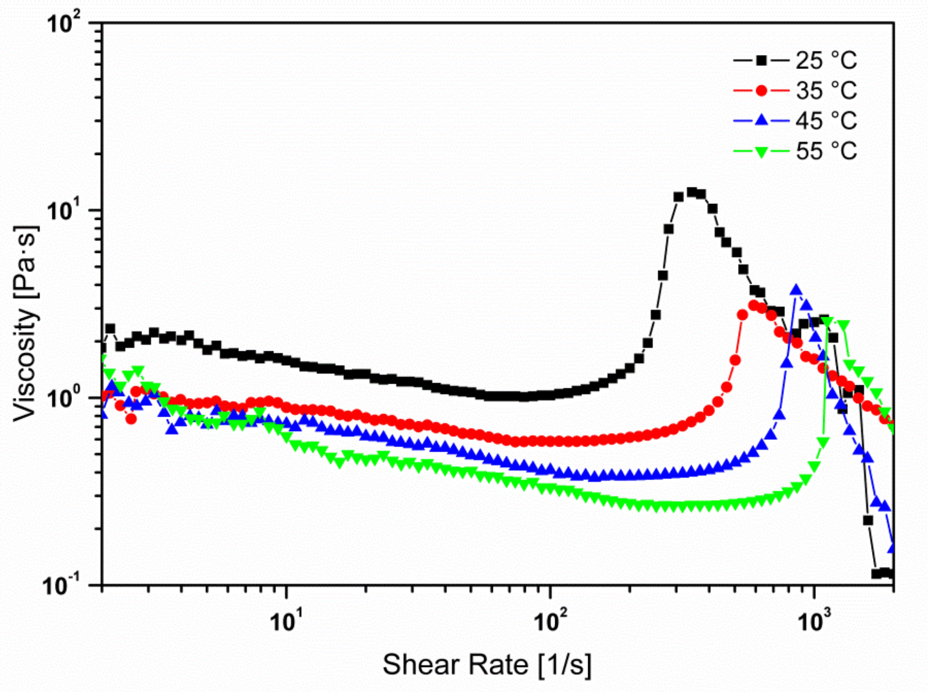


Figure 9.4 20% fumed silica STF with different percentage of 100cst silicone oil with PEG as the liquid medium

The effect of different concentrations of silicone oil in PEG was also seen on the temperature dependent behavior of STF. Figure 9.5 shows that as the temperature is increased from 25^0C to 55^0C, the value of the critical shear rate increases a lot and that of the critical viscosity decreases. It is evident that as temperature increases the strength of hydrogen bonding between the fumed silica particles and PEG molecules decreases and Brownian forces/repulsive forces increases [20-24] resulting in a decrease in low shear viscosity and the requirement of a large shear rate for formation of hydrocluster. As a result, for all concentrations, the critical viscosity is inversely proportional and value of critical shear rate is directly proportional to the temperature. It is interesting that silicone oil with PEG as the liquid medium to some extent decrease the effect of high temperature on viscosity of the STF i.e for 15% and 20% of silicone oil/PEG STF, the rate of decrease of critical viscosity at 45^0C and 55^0C is less. Temperatures higher than 55^0 C have not been probed as due to a very low viscosity of the samples at a higher temperature there is a chance of the sample to be ejected out from the plate of rheometer resulting in inexact rheological measurements.

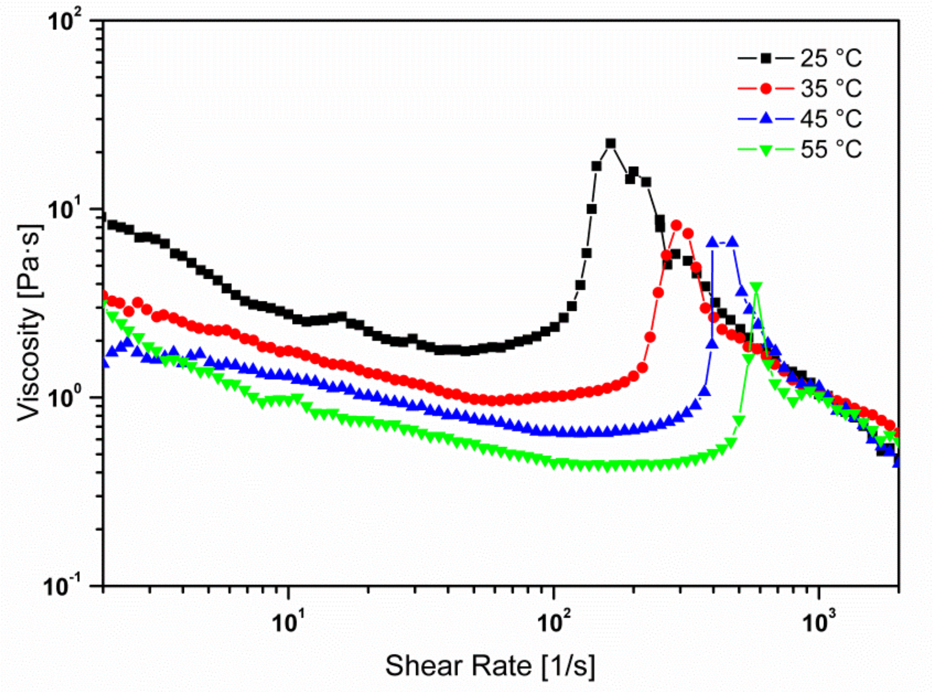


(a)



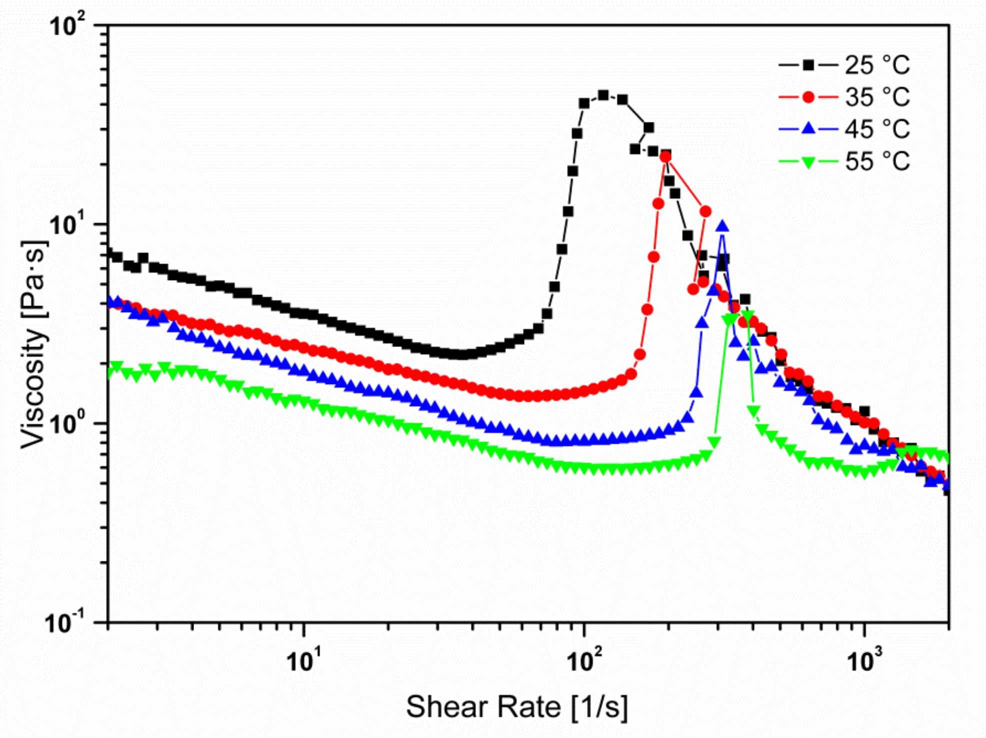
Viscosity [Pa·s]
Shear Rate [1/s]
10^{-1}
10^{0}
10^{1}
10^{2}
10^{1}
10^{2}
10^{3}
25 °C
35 °C
45 °C
55 °C

(b)



Viscosity [Pa·s]
Shear Rate [1/s]
10^{-1}
10^{0}
10^{1}
10^{2}
10^{1}
10^{2}
10^{3}
25 °C
35 °C
45 °C
55 °C

(c)



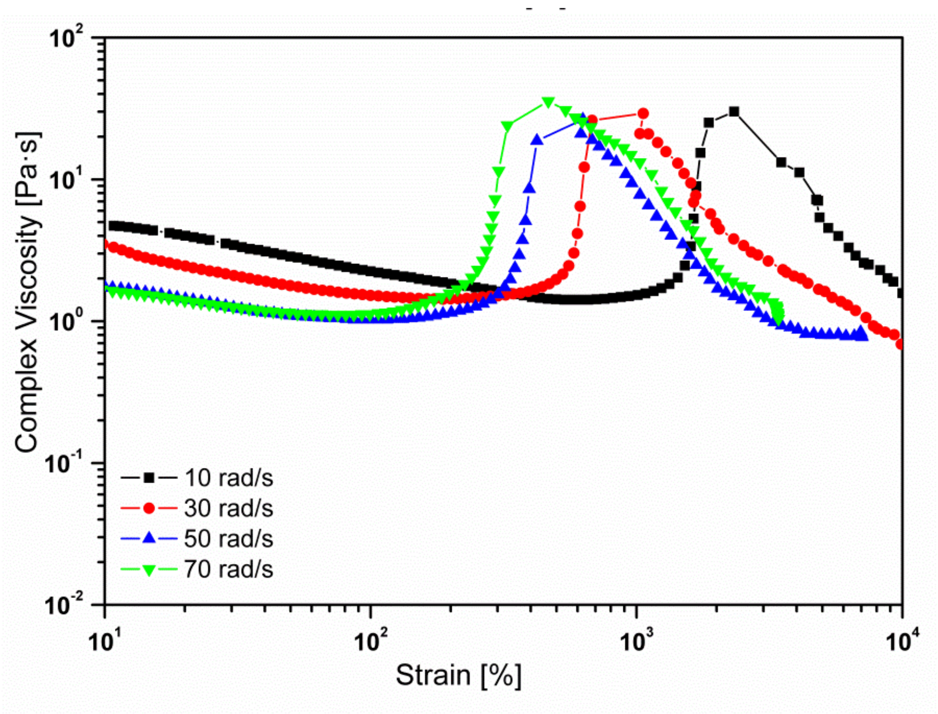
(d)

Figure 9.5 Effect of temperature on 20% fumed silica STF containing a) 0% b) 10 % c) 15% and d) 20% silicone oil with PEG as liquid medium

Dynamic state measurements

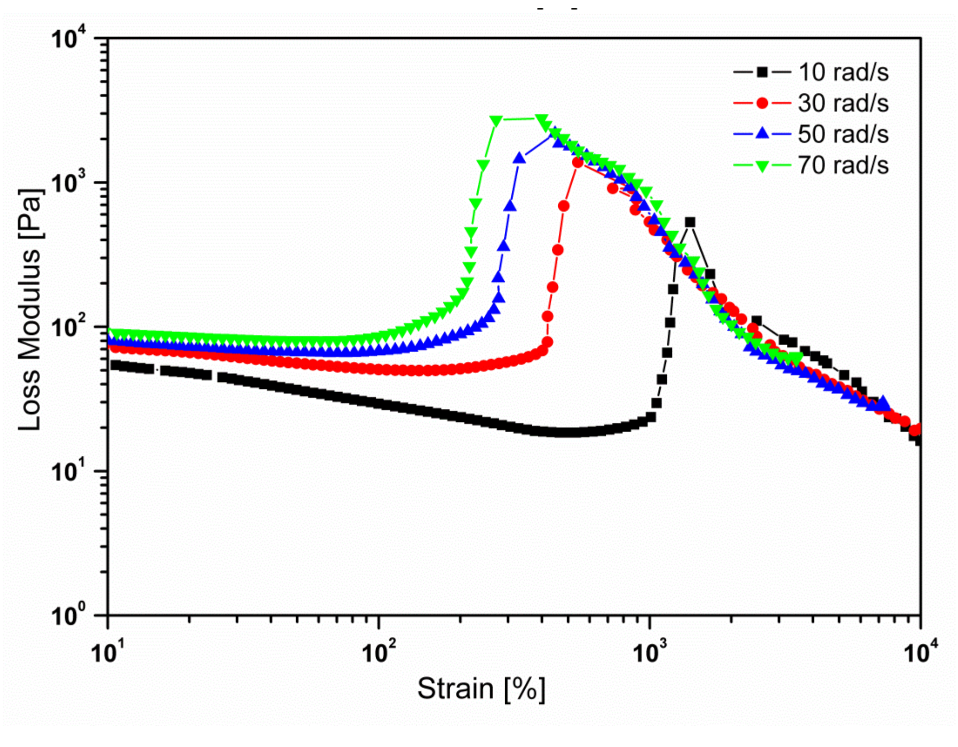
The dynamic rheological parameters of maximum concentration of 20% silicone oil STF were shown in Figure 9.6 depicting the complex viscosity, G' and G". Complex viscosity shows a slightly decreasing trend with increasing frequency but is eventually stable at higher frequencies of 50 rad/s and 70 rad/s (Figure 9.6a). As compared to the steady-state viscosity (45 Pas), complex viscosity (40 Pas) of 20% silicone oil STF only slightly decreases. The probable reason for this slight decrease, a contrast to a large decrease in the values for other STF studied (Chapters 5, 6, 7 and 8) is that in the dynamic state, the highly elastic nature of silicone oil prevents breaking of particle clusters. Complex viscosity profiles for 0%, 10% and 15% concentration are shown in Figure 9.7. At high strains, as concentration increases, the critical value of complex viscosity increases for all frequencies. G' and G" profiles at different frequencies are shown in Figure 9.8 and 9.9 respectively. Thus, the dynamic tests result for all samples are quantitatively similar and are in line with the results available in the literature that the STF exhibits strain thickening at critical strain amplitude that is inversely proportional to the frequency of oscillation [25-29].

It can be seen in Figures 9.8 and 9.9 that G" and G' in strain sweep at all four frequencies, again show three zones similar to that in complex viscosity profile. Initially G" slightly decreases with almost linear behavior with an increase in shear strain, then at a critical strain, a smooth increase is noted till a maximum is reached due to an increase in cluster volume, after which decrease in G" starts due to rupture of clusters at high strains (Figure 9.8). Furthermore, a slight increase in loss modulus can be seen by increasing the concentration of silicone oil. From the dynamic rheology profiles of Figure 9.9, it is apparent that unlike the response shown by loss modulus, the storage modulus follows a non-linear response at low strains till critical strain and beyond critical strain, non-linearity increases for both moduli characterized by the onset of the strain-dependent behavior typical of viscoelastic nature of shear thickening fluids. The shear-strain at which an increase in both the moduli starts is in accordance with that at which the value of complex viscosity begins to increase with the plots of the more concentrated sample showing an earlier fall. Similar to the loss modulus, the elastic modulus also increases as frequency increases but it is more sensitive to frequency and much more sensitive to the concentration of silicone oil at high strains. Thus there is a large increase in elastic modulus after critical strain as the concentration of silicone oil increases. For all samples, in the range of investigated frequencies, the loss modulus is higher than the storage modulus indicating stable and viscoelastic liquid characteristic. Briefly, the results indicate that on shearing suspension more quickly, it becomes more elastic and viscous. Moreover, blending has provided a means to modify the moduli. Also, the steady-state and dynamic rheological tests were found to produce consistent and reproducible results showing that the suspensions are highly homogenous.



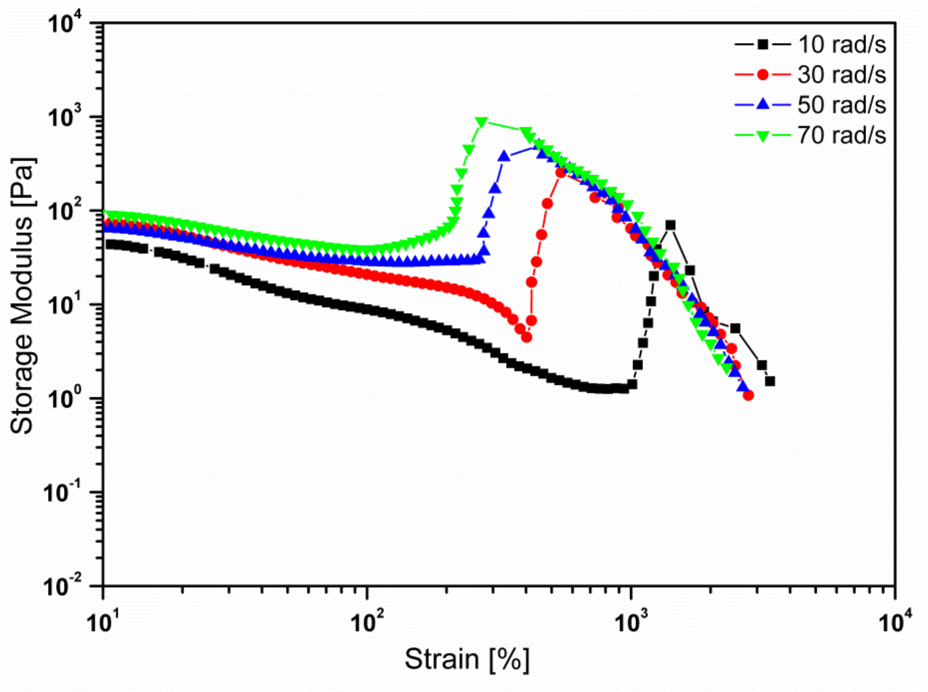
Complex Viscosity [Pa·s]
Strain [%]
10 rad/s
30 rad/s
50 rad/s
70 rad/s

(a)



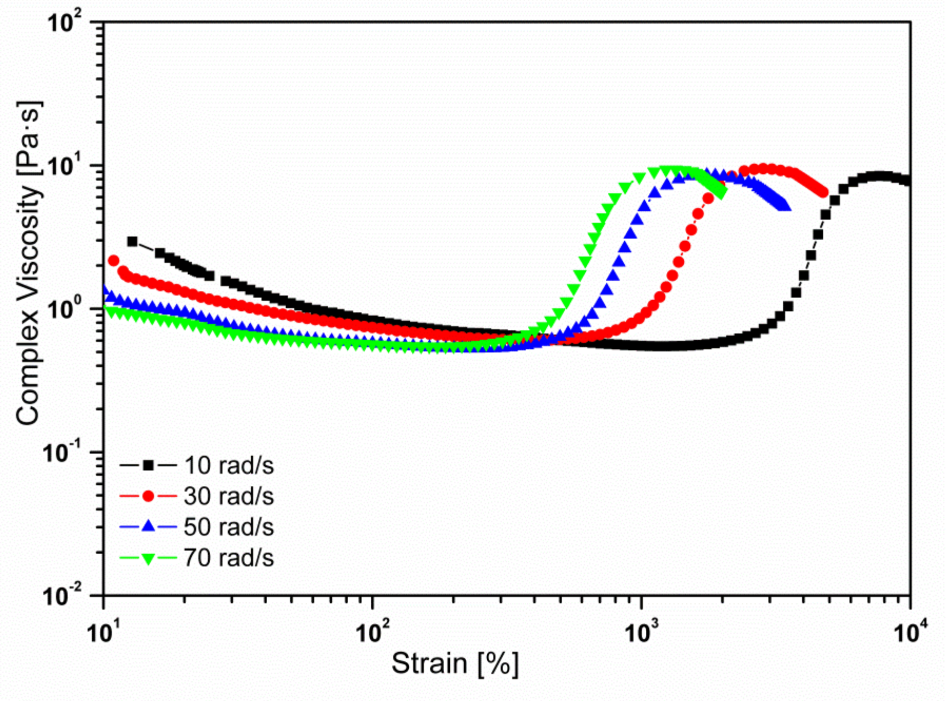
Loss Modulus [Pa]
Strain [%]
10 rad/s
30 rad/s
50 rad/s
70 rad/s

(b)

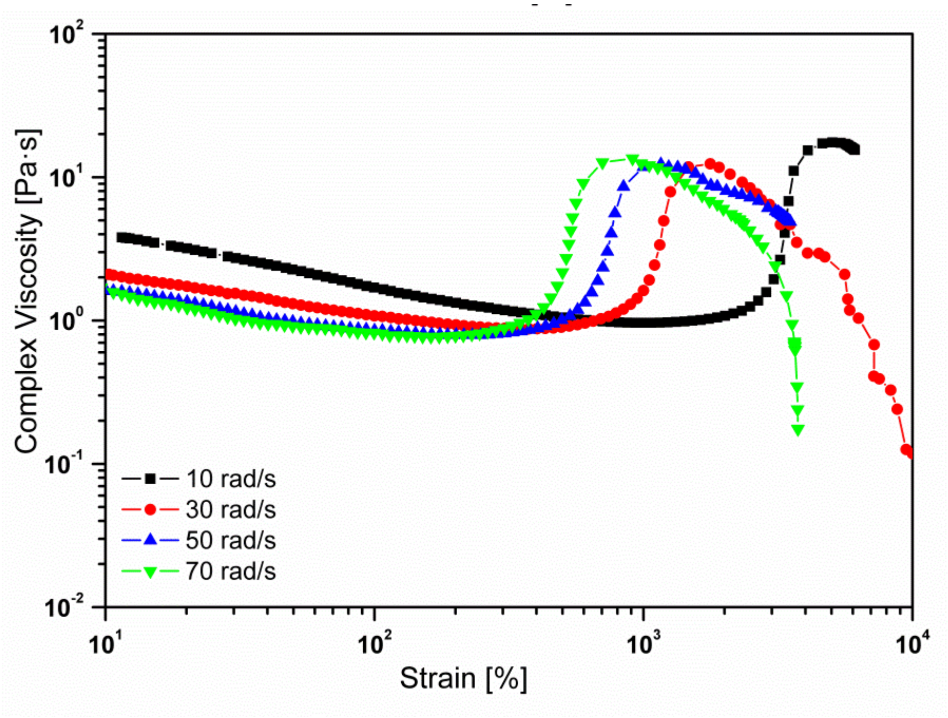


(c)

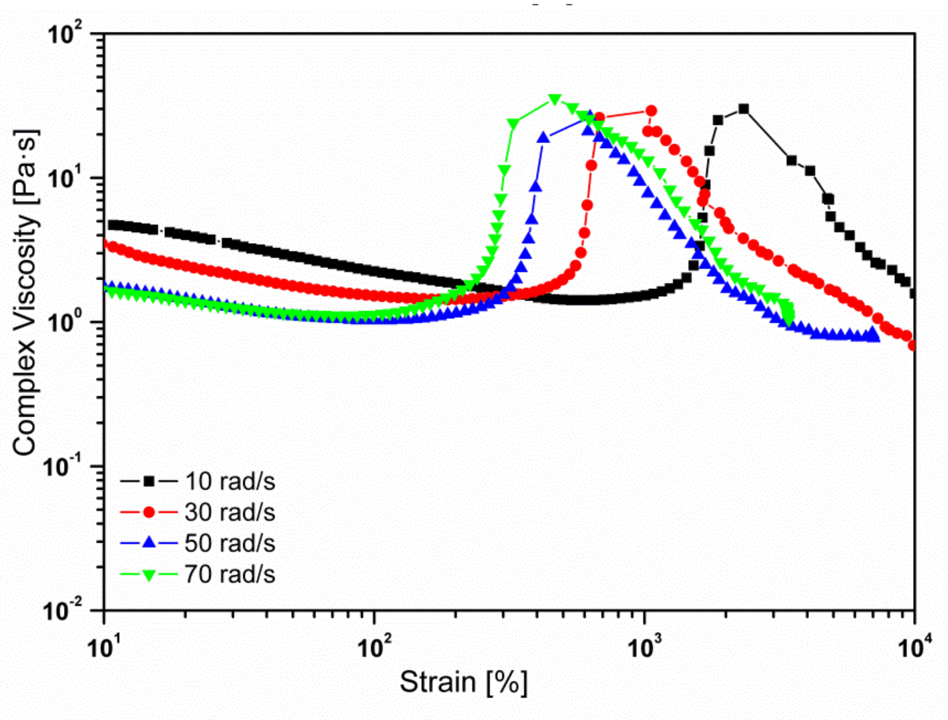
Figure 9.6 a) Complex viscosity, b) loss modulus, and c) storage modulus at different frequencies for 20% silicone oil with PEG as the liquid medium



(a)

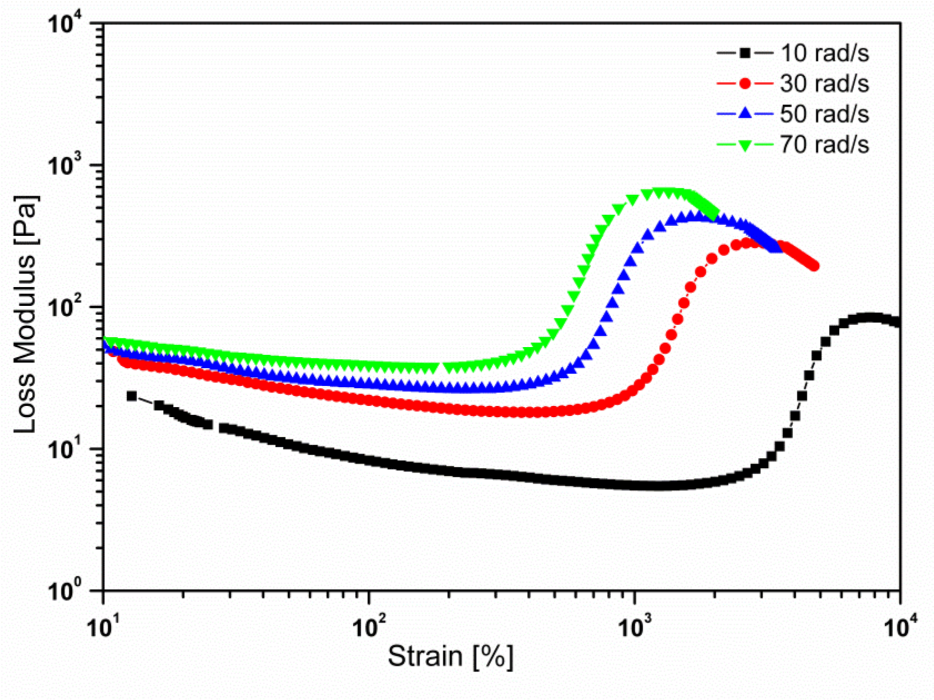


(b)



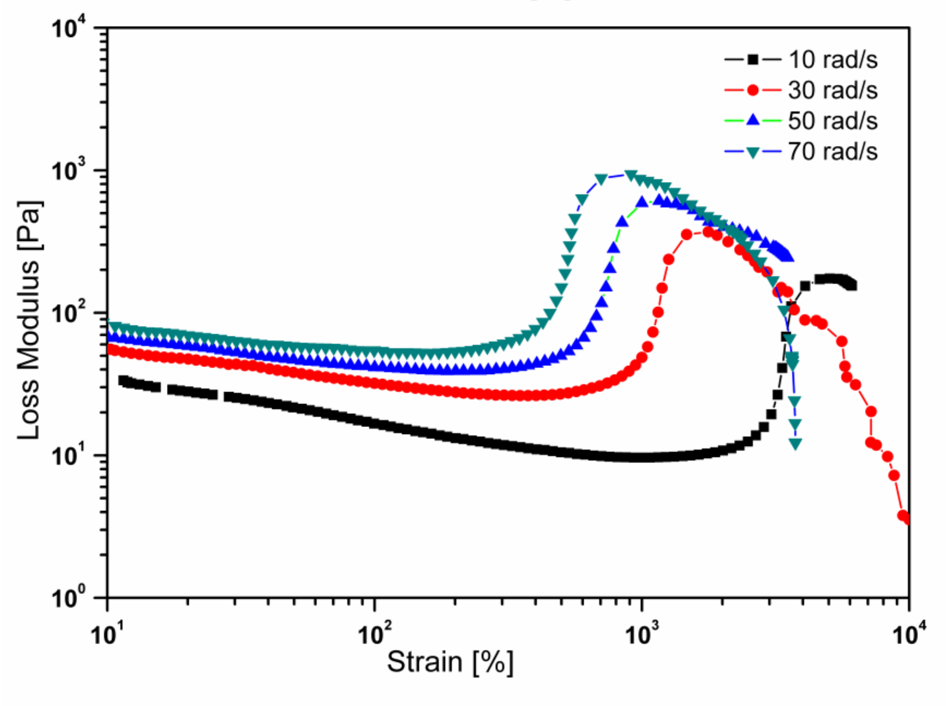
(c)

Figure 9.7 Comparison of complex viscosity at different frequencies for a) 0%, b) 10% and c) 15% silicone oil with PEG as the liquid medium



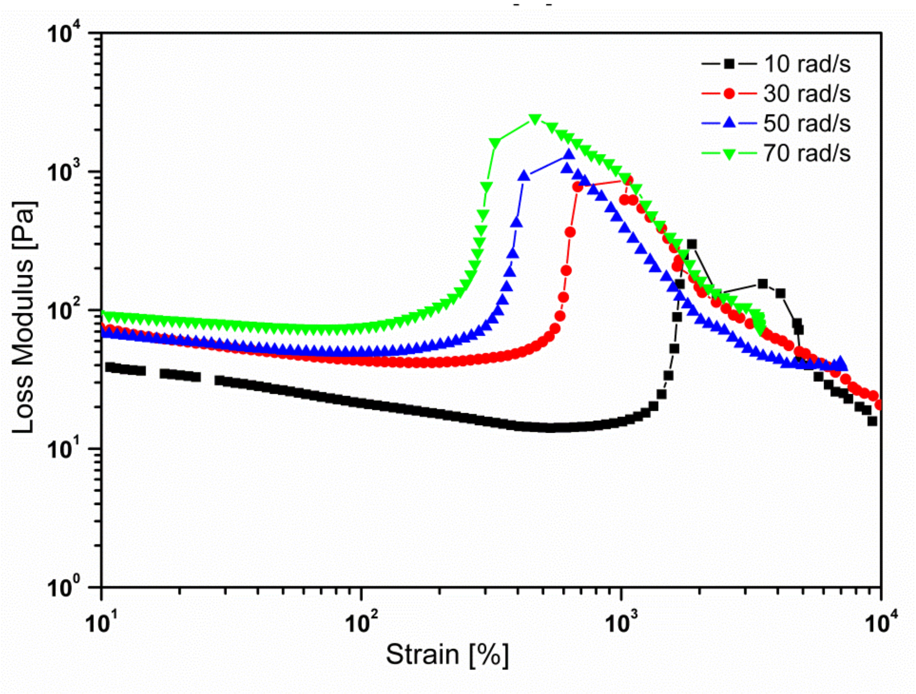
10⁴
10³
10²
10¹
10⁰
Loss Modulus [Pa]
10¹
10²
10³
10⁴
Strain [%]
10 rad/s
30 rad/s
50 rad/s
70 rad/s

(a)



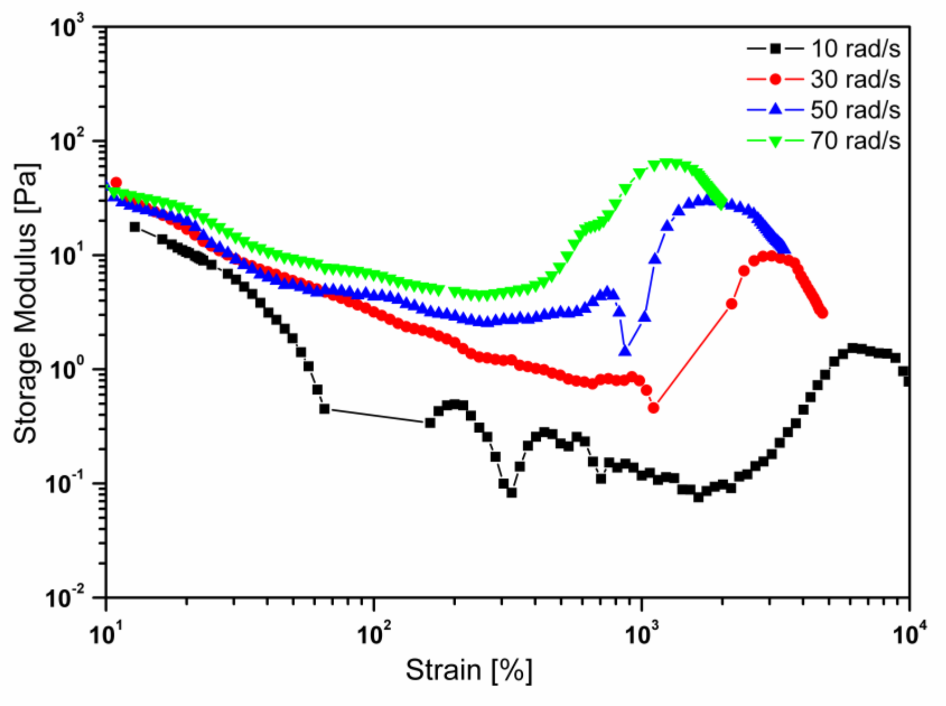
10⁴
10³
10²
10¹
10⁰
Loss Modulus [Pa]
10¹
10²
10³
10⁴
Strain [%]
10 rad/s
30 rad/s
50 rad/s
70 rad/s

(b)

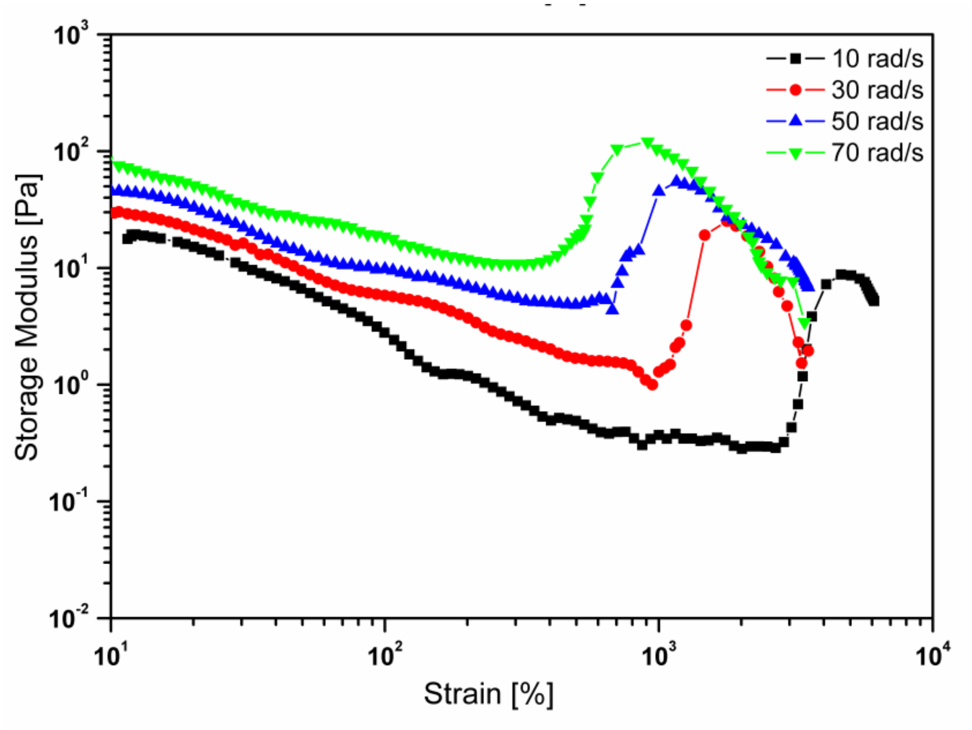


(c)

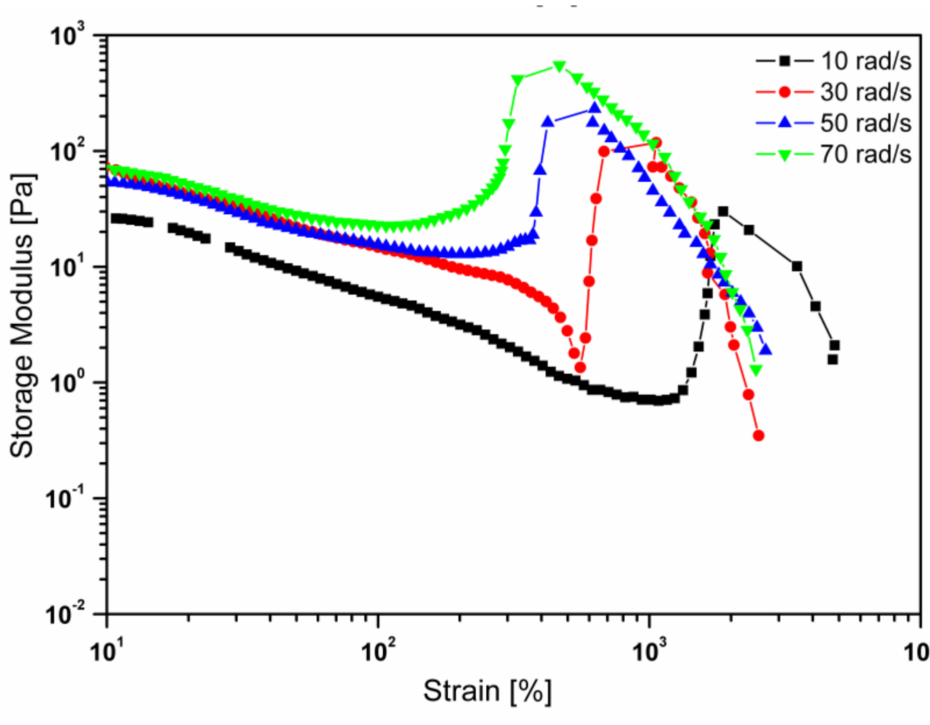
Figure 9.8 Comparison of loss modulus at different frequencies for a) 0%, b) 10% and c) 15% silicone oil with PEG liquid medium



(a)



(b)



(c)

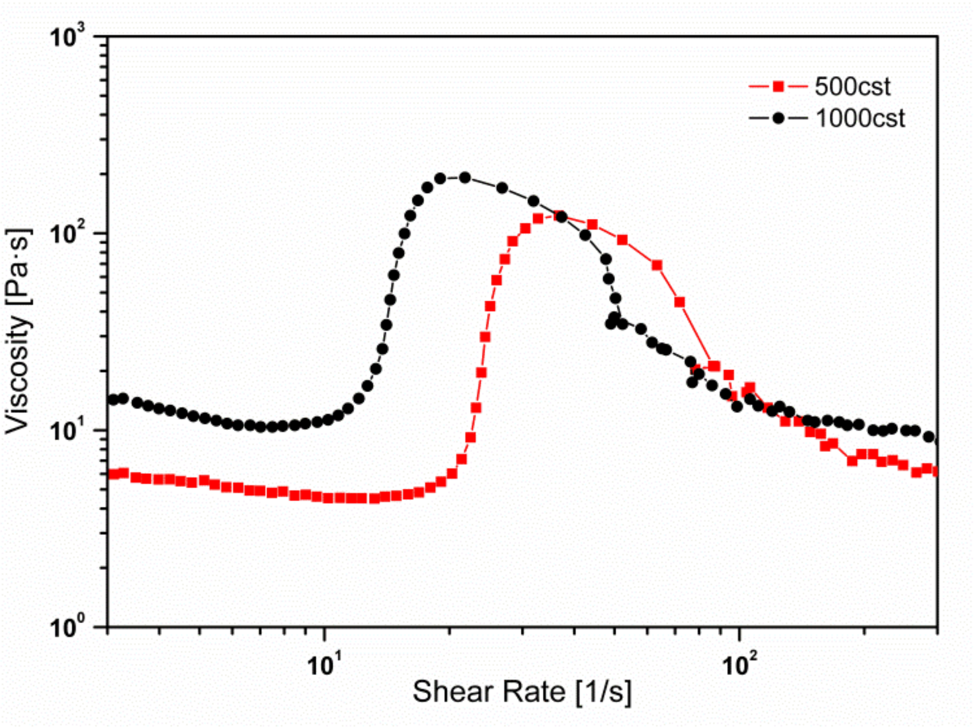
Figure 9.9 Comparison of storage modulus at different frequencies for a) 0%, b) 10% and c) 15% of silicone oil with PEG liquid medium

9.3.2.2 Comparison of STF with 15% silicone oil of viscosity 500cst and 1000cst compounded with PEG

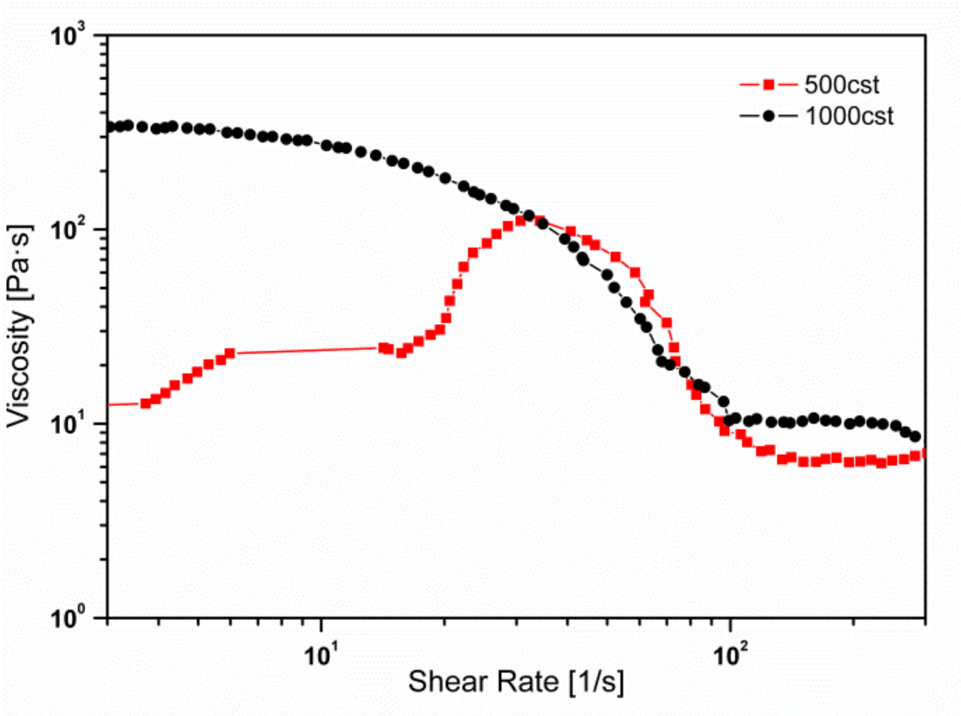
The steady-shear viscosity and dynamic viscoelastic behavior were measured for suspensions of fumed silica-silicone oil compounded PEG STF having 10% and 15% of silicone oil as solvent, where two types of silicone oil of kinematic viscosity: 500cst and 1000cst are used. For 100cst silicone oil the maximum concentration of PEG that can be replaced is 20%. However, for 500cst and 1000cst the maximum concentration is only 15%.

Steady-state measurements

The steady-state rheology at 25^0C and 35^0C of both 500cst and 1000cst of the maximum concentration of 15% is shown in Figure 9.10. It can be observed that there is about 2 times increase in the overall values of the viscosities including the critical viscosity for 1000cst (200 Pa.s) than 500cst (120 Pa.s). At 35 ^{0}C, 1000cst shows shear thinning behavior and there is not much difference in critical viscosity for 500cst silicone oil (120 Pa.s to 110 Pa.s) and critical shear rate (12 s^{-1} to 13 s^{-1}) compared to 25^0C as shown in Figures 9.10a and b. Additionally, at 45^0C (Figure 9.11a), 1000cst shows harder gel-like structure as is evident from high values of viscosity at low shear rates compared to 35^0C followed by shear thinning. Similarly, 500cst silicone oil STF also show very high values of viscosities compared to 35^0C at initial shear rates, although some shear thickening behavior still remains in 500cst STF. Therefore, silicone oil of viscosity 1000cst at a temperature of 35^0C typically gels with a very high viscosity at low shear rates and shear thinning behavior. Thus, as chains of high viscosity silicone oils of higher molecular weight are more entangled, thus result in a gel like structure. Silicone oil of 500cst however, has a significantly higher critical viscosity and critical shear rate and show stability up to 45^0C.

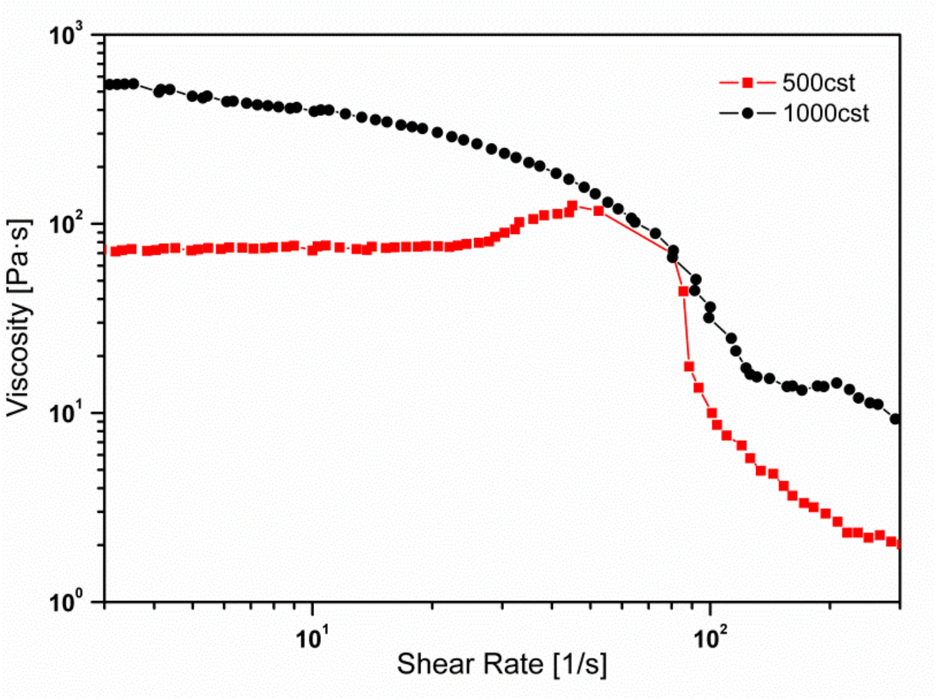


(a)

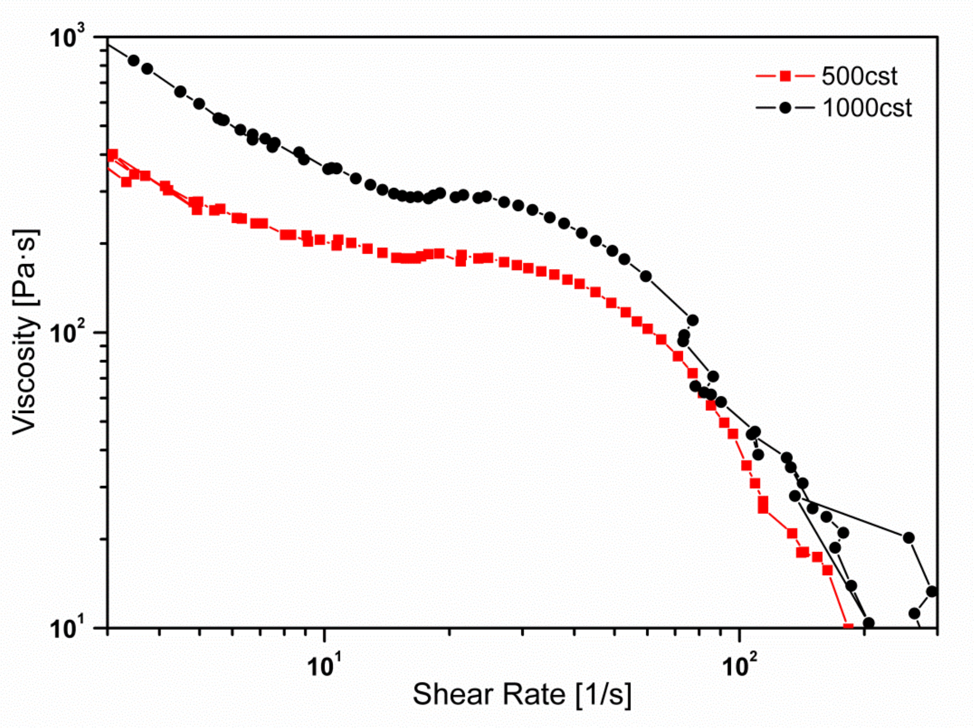


(b)

Figure 9.10 Steady-state rheology of 15% silicone oil at a) 25 ^{0}C and b) 35 ^{0}C



(a)



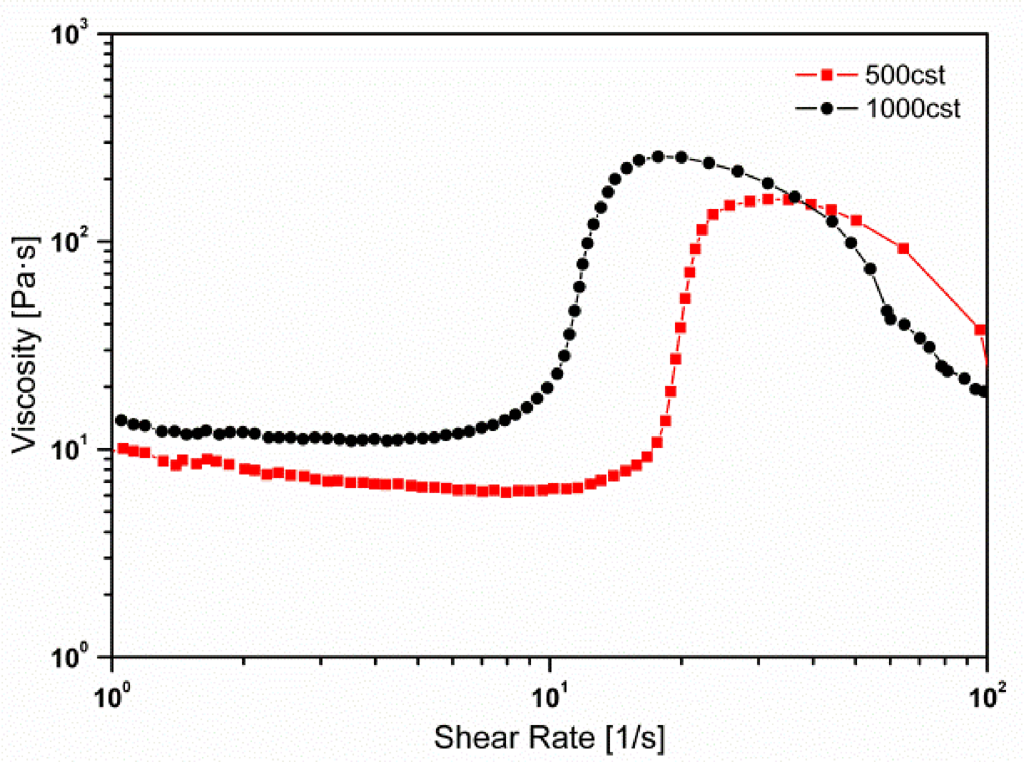
(b)

Figure 9.11 Steady-state rheology of 15% silicone oil at a) 45 ^{0}C and b) 55 ^{0}C

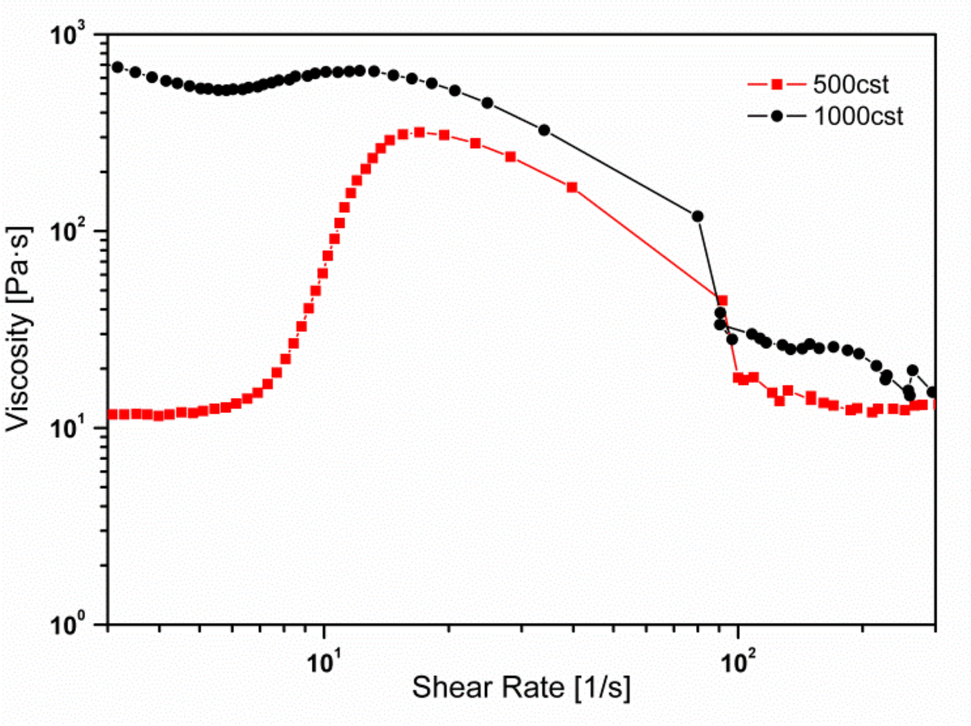
At 55 ^{0}C, however, 500cst also shows shear thinning behavior as depicted in Figure 9.11b. This is indicative of particle clustering resulting in a 3-D network of a gel or STF are considered to be oversaturated STF. The reason for this type of rheological behavior is postulated as that the strength of hydrogen bonding between fumed silica and PEG molecules decreases as temperature increases, this leads to initial flocculation and or aggregation of particles resulting in a gel-like structure. Moreover, for 1000cst silicone oil, the gel structure is more pronounced due to a more branched morphology of its molecules compared to 500cst silicone oil. At a low temperature of 15^{0}C, both 500cst and 1000cst silicone oil STF show large viscosity (Figure 9.12a). However, as compared to 25 ^{0}C again, there is not much difference in the values i.e. 200 to 270 Pa.s for 1000cst STF and 120 to 160 Pa.s for 500cst STF. Moreover, at 5^{0}C, only 500cst STF show shear thickening (350 Pa.s) at 4 s^{-1} (Figure 9.12b). At low temperature, due to a decrease in repulsive forces, hydrocluster formation intensifies and size of hydroclusters increases resulting in very small values of critical shear rate along with high values of critical viscosity. Thus from temperature studies, it can be concluded that for 15% concentration of 1000cst STF is only stable up to 35^{0}C and 15 ^{0}C at high and low side temperature, respectively whereas 500cst is stable up to 45 ^{0}C at the high side of temperature and up to 5 ^{0}C at low temperature side. Also, interestingly the high value of critical viscosity of both STF at different temperatures show a fairly low sensitivity as a function of temperature.

Dynamic state rheology

Dynamic state rheology of STF consisting of highest concentration i.e. 15% of both 500cst and 1000cst silicone oil STF (Fig 9.13a and b) shows that at low strains storage modulus is slightly larger than loss modulus for 1000cst which indicates gel-like behavior but as the strain increases viscous nature increases and loss modulus becomes greater than storage modulus. Moreover, as frequency value increases the value of all parameters increases at a declining rate at higher frequencies but the difference in values of parameters between 500 and 1000cst silicone oil decreases. Thus, at high frequencies (50 rad/s and 70 rad/s) 15% of both 1000cst and 500cst STF behaves in a similar manner under dynamic strain sweep. Moreover, as at frequency values of 50 and 70rad/s, the dynamic parameters do not change much, hence, 70rad/s can be assumed as the critical value of the frequency for 15% silicone oil STF. There is a slight decrease in values of complex viscosity (Figure 9.13c) as compared to steady-state viscosity with much more decrease for 1000cst silicone oil STF, which shows the sensitivity of 1000cst silicone oil STF towards the flow behavior.

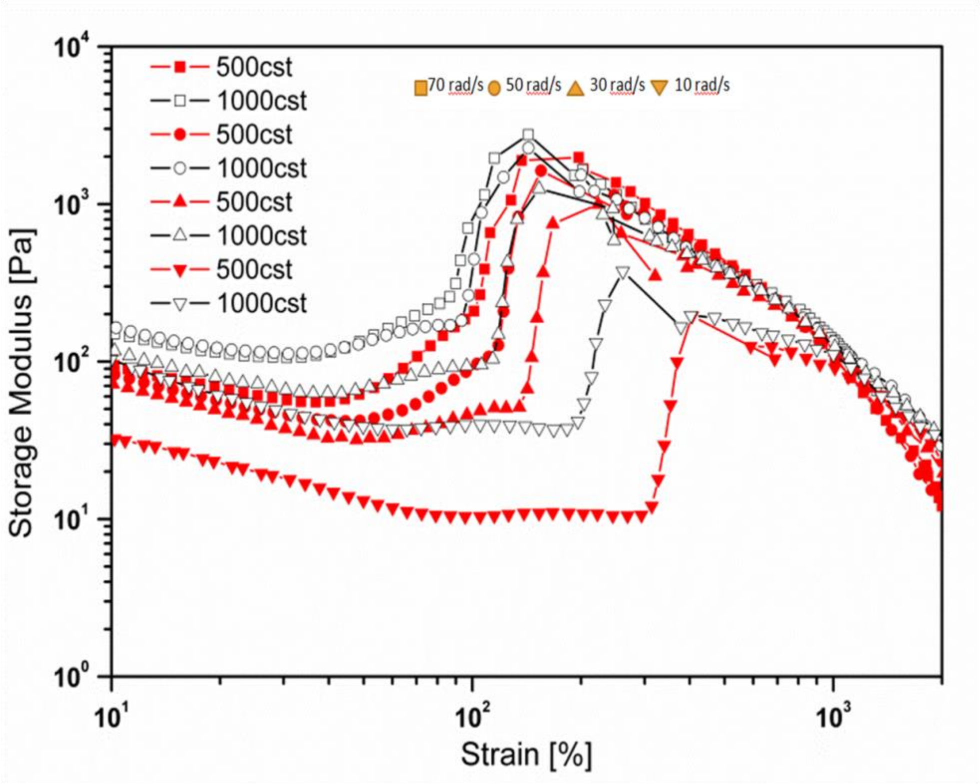


(a)

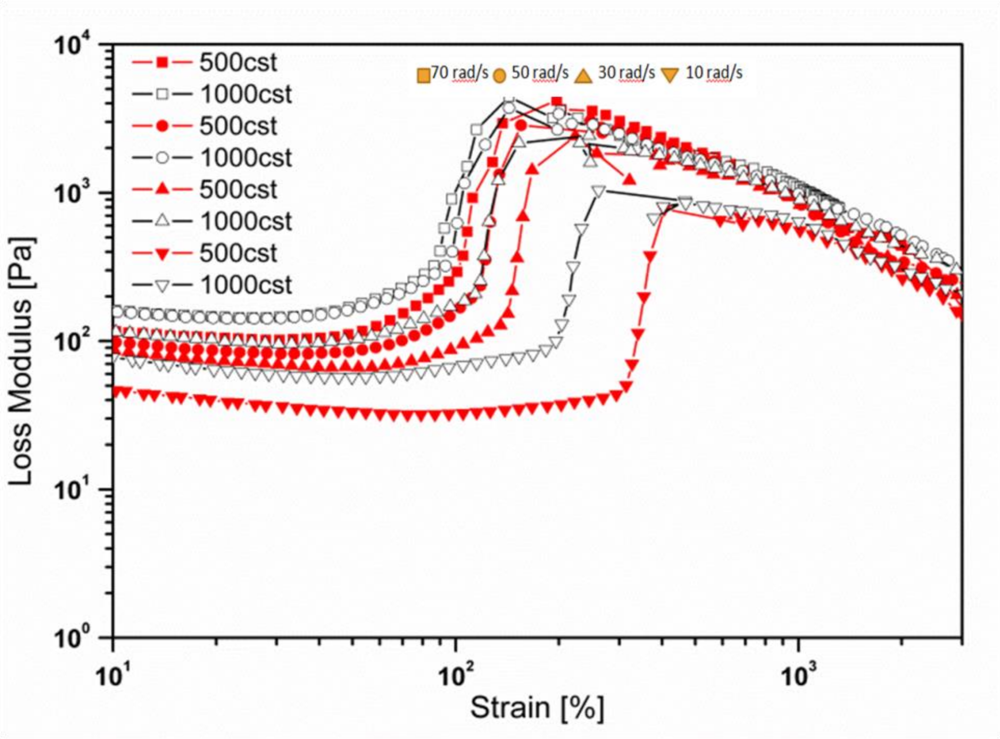


(b)

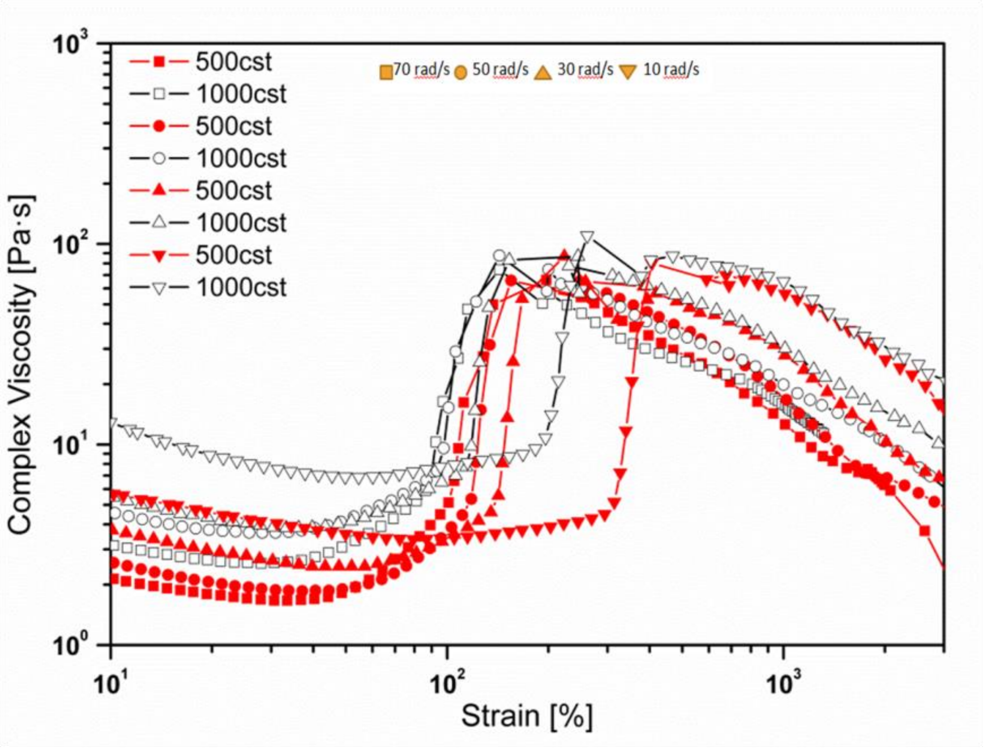
Figure 9.12 Steady-state rheology of 15% silicone oil at a) 15 ^{0}C and b) 5 ^{0}C



(a)



(b)



(c)

Figure 9.13 Dynamic-state rheology showing profiles of a) storage modulus b) loss modulus and c) complex viscosity of 15% silicone oil at different constant frequencies

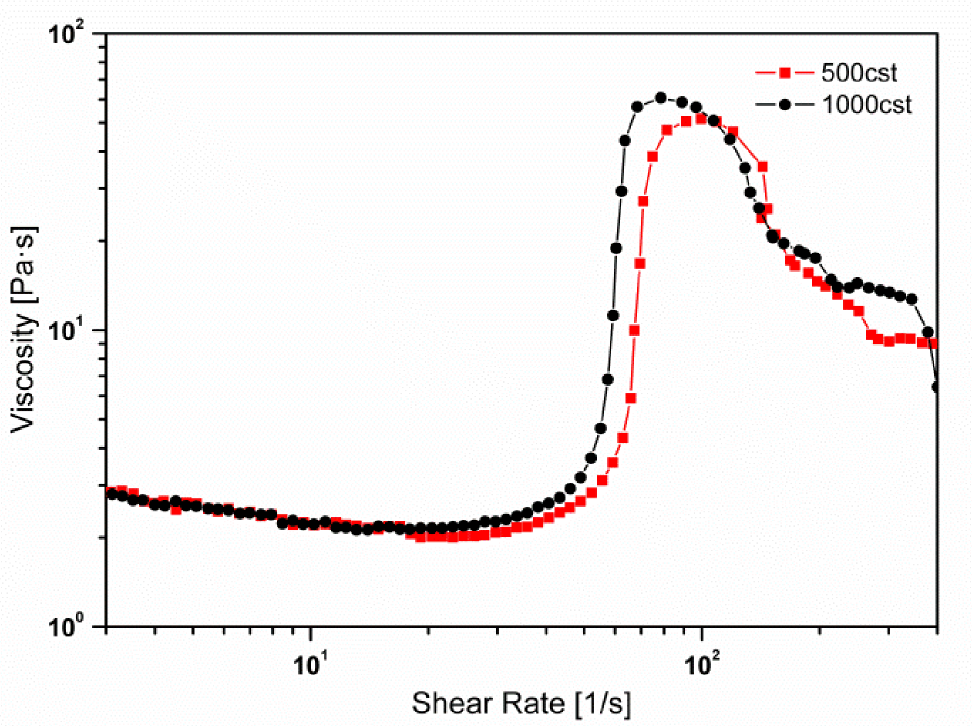
9.3.2.3 Comparison of STF with 10% silicone oil of viscosity 500cst and 1000cst compounded with PEG

Steady-state measurements

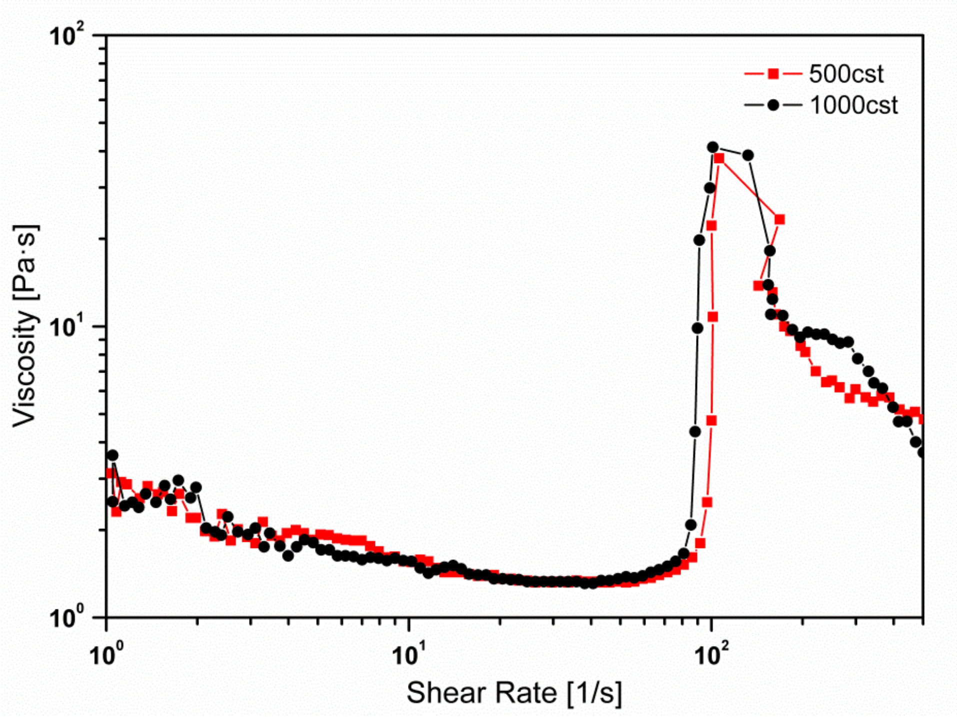
Steady-state rheology of 10% concentration of silicone oil STF at 25^0C and 35^0C shows that there is not much difference in critical viscosity and critical shear rate for two different viscosity silicone oil (Figure 9.14a and b). At 25^0C critical value of viscosities are 60 and 50 Pa.s for 1000cst and 500cst silicone oil STF, respectively whereas critical shear rate is almost same for both i.e 40 s^{-1}. Similarly, at 35^0C critical viscosity and critical sear rate values are same for both STF at 45 Pa.s and 70 s^{-1} respectively. These results points out an important conclusion that 500cst silicone oil STF show more shear thickening properties than 1000cst silicon oil STF.

As temperature increases the viscosity decreases for both silicone oil STF (Figures 9.15a and b). Also, a contrasting behavior is seen that critical shear rate for 500 cst is less than 1000cst at both 45^0C and 55^0C, however, the critical viscosity for 500 cst is more than 1000 cst at 55^0C which state that at high temperature, gel behavior increases and much increase is encountered for high viscosity silicone oil.

The critical viscosity at low temperatures of 15^0C and 5^0C is comparable for both silicone oil at 220 and 101 Pa.s respectively as shown in Figures 9.16a and b.

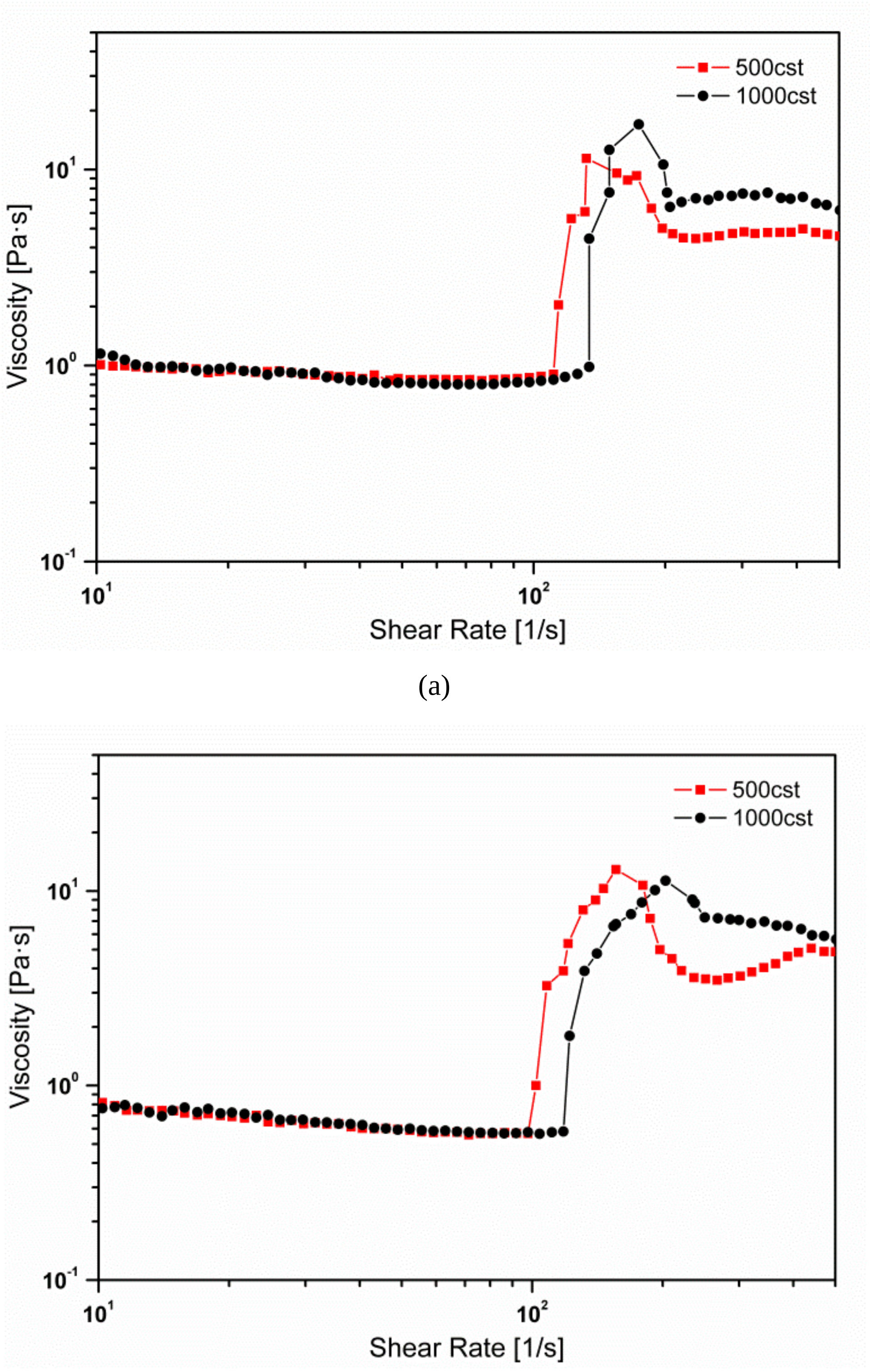


(a)



(b)

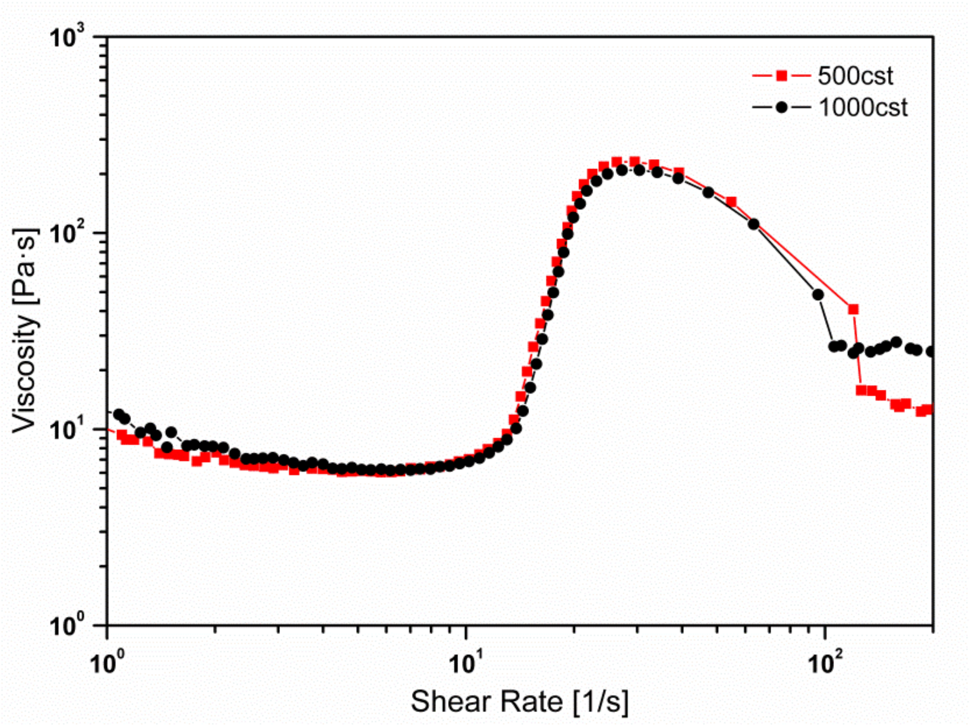
Figure 9.14 Steady-state rheology of 10% silicone oil at a) 25 ^{0}C and b) 35 ^{0}C



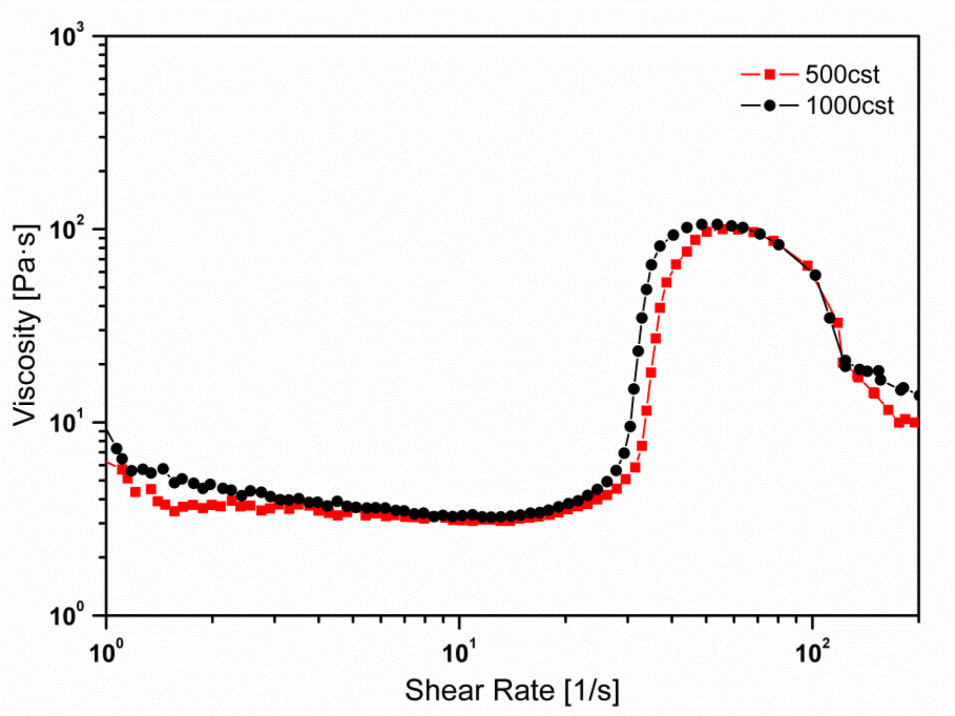
(a)

(b)

Figure 9.15 Steady-state rheology of 10% silicone oil at a) 45 ^{0}C and b) 55 ^{0}C



(a)



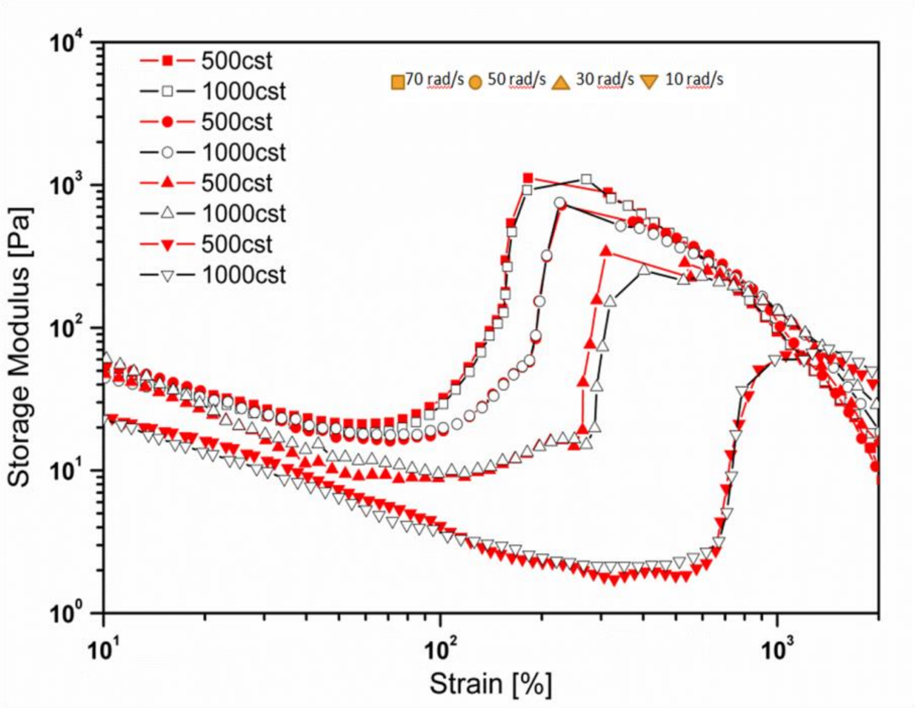
(b)

Figure 9.16 Steady-state rheology of 10% silicone oil at a) 5 ^{0}C and b) 15 ^{0}C

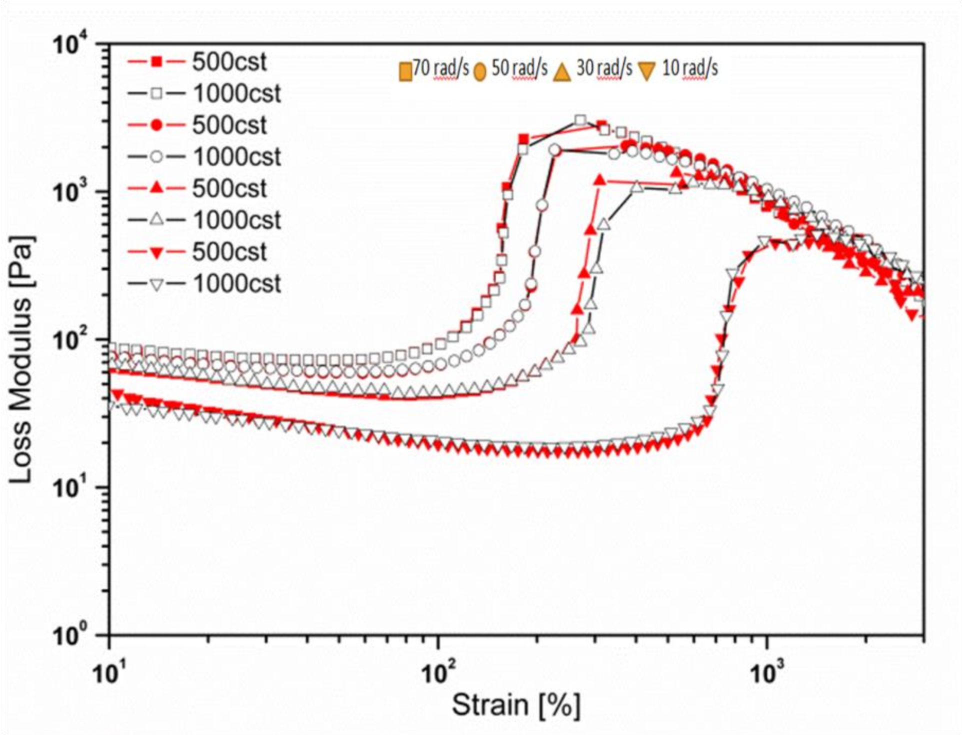
Consequently, at 10% concentration, again 500cst is more stable with higher shear thickening properties at both high and low temperatures. Moreover, in contrast to 15% concentration the 10% concentration of STF is stable at all temperatures studied.

Dynamic state rheology

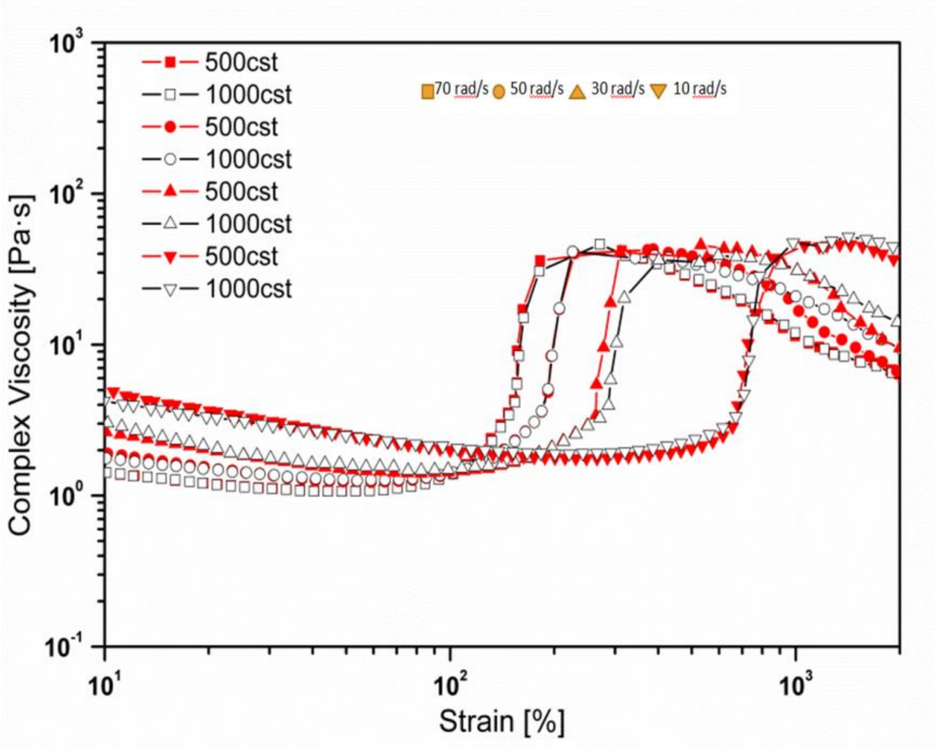
Again, similar to steady-state rheology there is not much difference in values of critical complex viscosity (Figure 9.17c) between two different viscosity silicone oil although complex viscosity is slightly less than steady-state viscosity. At 10% concentration for both 500cst and 1000cst silicone oil STF, the critical values of storage modulus (G') and loss modulus (G″) (Figures 9.17a and b) do not become constant at even high frequencies and keep on changing till the maximum value of frequency studied (70 rad/s), which is in contrast to 15% concentration i.e. the difference in the values of both moduli decrease with respect to an increase in the constant value of frequency but do not approach constant values. This may be due to the fact that for low concentration of 10% silicone oil the critical frequency value is higher than 70rad/s.



(a)



(b)



(c)

Figure 9.17 Dynamic-state rheology showing profiles of a) storage modulus b) loss modulus and c) complex viscosity of 10% silicone oil at different constant frequencies

9.4 Conclusion

Overall, it can be concluded that the STF with silicone oil, has a higher maximum viscosity and the greater shear thickening effect than the referential sample based only on PEG200 as the liquid medium. Steady-state results shows that although PEG forms hydrocluster due to polymer bridging between the particles, silicone oil due to its more branched structure results in the large hydroclusters similar to those formed in absence of it but typically at much lower particle concentration, which leads to a high extent as the concentration of silicone oil increases. At a very high concentration of silicone oil shear thickening decreases possibly due to less amount of PEG which cannot modify silicone oil for bridging purpose. Therefore, only up to 20% for 100cst and 15% concentration of both 1000 and 500cst silicone oil STF are stable. Steady-state viscosity increases and critical shear rate decreases on increasing concentration of silicone oil.

Addition of 20% silicone oil (100cst) to PEG/fumed silica STF results in a tremendous increase (about 300%) in the critical viscosity and only 40% decrease in critical shear rate. At high temperatures (45^0 and 55^0C), the critical viscosity drops to very low values. Thus, in general, STF material developed may not find application overall temperature range. At high silicone oil concentration complex viscosity, loss modulus and storage modulus increase and critical strain decrease; A large value of both the moduli is obtained as the frequency of oscillation increases which suggests that the suspension would be capable of showing shear thickening under a high-velocity impact. 10% of 500cst silicone oil as suspension medium is more stable than 1000cst at both high and low temperatures. 15% of silicone oil is less stable at low and high temperatures, and this instability further increases for 1000cst silicone oil. 1000cst shows gel (shear thinning) like behavior at even a slightly higher temperature of 35^0C. This is also confirmed by dynamic rheology as storage modulus is greater than loss modulus at low strains. However, for 10% concentration, both silicone oil STF are stable as they do not show flocculation or gel-like behavior. Moreover, 10% of 500cst silicone oil as a suspension medium is more stable than 1000cst. Thus, limited by the flocculation and formation of gel-like structure, the disadvantage of high viscosity silicone oils results in poor performance at high as well as low temperatures. 1000cst silicone oil STF readily becomes flocculation hence the retention of STF properties of silicone oil of 500cst STF is higher than that of 1000cst STF. The improvement in properties on the addition of silicone oil is due to the synergy between cross-linked PEG/ silicone oil as the liquid medium and strongly interacting fumed silica nanoparticles resulting in a dramatic increase in shear thickening. When comparing STF without silicone oil with the STF containing silicone oil, a large increase in elasticity for the latter is observed and then implies that shear thickening properties with silicone oil replacing some concentration of PEG is superior. In dynamic strain sweep for 1000cst silicone oil STF, storage modulus is greater than loss modulus at low strains which indicate some gel formation, however, at high strains and also for all STF loss modulus is greater than storage modulus.

These results are very interesting and indicate that silicone oil-PEG as a dispersion medium for a shear thickening fluid system will play a major role in achieving enhanced shear thickening properties of the STF. The chemical and physical structure of additives significantly affect the shear thickening parameters and stability. Thus, the required pattern of shear thickening behavior of STF is possible to obtain by controlling the rheological properties depending on the use of suitable additives and compositions. Shear thickening properties, such as high critical viscosity, at an appreciable shear rate and elasticity, can, therefore, be modulated by varying the amount of additives.

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Chapter 10 Effect of hydrophilicity of fumed-silica on rheology of STF

From the studies reported in preceding chapters, it was concluded that shear thickening suspensions can be designed with different nanoparticles and solvents to result in various useful material properties. One of the most significant characteristics of these complex fluids (STF) is the molecular-level integration of the organic and inorganic phases by physical interactions. Further to support the point, the effect of hydrophilicity of fumed silica particles has been studied in this chapter. STF were processed by both hydrophilic and hydrophobic fumed silica particles as dispersed particles. PEG200 having hydrophilic character and PPG425 having both hydrophilic and hydrophobic character have been used as the dispersion medium.

10.1 Introduction

In order to manufacture a STF that suits a required application, it is crucial to understand the effect of material properties systematically on the effect of shear thickening rheology. For instance, a STF that thickens at very low shear rate may be used for sensitive applications such as low impact situations whereas, STF that thickens at high shear rates would be used optimally for high impact scenario or ballistic impacts. Till date, STF composed of hydrophilic silica particles and hydrophilic ionic liquid PEG has been studied [1-3]. These dispersed phases contain hydroxyls or polar groups on the surface, which makes the particles to disperse non-flocculantly in the dispersion medium containing hydroxyl or polar group. However, dispersed phases that do not contain hydroxyl or polar groups have not been studied much. Raghvan (2000) found that hydrophobic fumed silica is largely capable of gelling polar PEG200. Hydrophobic fumed silica particles preferentially form the hydrogen bond with the surface silanol groups and form silica aggregates leading to flocculation and gelling [4]. However, Galindo-Rosales (2009) reported results showing non-flocculated sol with 10% hydrophobic silica containing non-polar groups on its surface dispersed in polar liquid [5]. Moreover, shear thickening properties increase significantly with favorable particle matrix interactions compared to non-interacting systems or systems having strong p-p interactions. This suggests that the polarity of the proximal chemical environment is critical affecting the shear thickening properties of the inorganic cluster. The objective of the present study is to investigate the effect of surface characteristics of two kinds of fumed silica (hydrophilic and hydrophobic) and polarity of PEG and PPG on the dynamic and steady-state rheology of STF. Comparing these data provides a better understanding of the effects of properties of particles and the importance of hydrophilicity of medium. Although much work has been done on hydrophilic fumed silica and PEG STF (FS+PEG), very few have been reported on hydrophobic fumed silica and PEG STF (HFS+PPG) and hydrophilic fumed silica and PPG STF (FS+PPG).

10.2 Processing

To prepare 20% of STF small amount of silica particles are added to PEG/PPG in steps with subsequent sonication by probe sonicator. Three samples were prepared: a) hydrophilic fumed silica and PEG (FS+PEG); b) hydrophobic fumed silica and PPG (HFS+PPG); and c) hydrophilic fumed silica and PPG (FS+PPG). Figure 10.1 shows the HFS+PPG STF and FS+PPG STF.

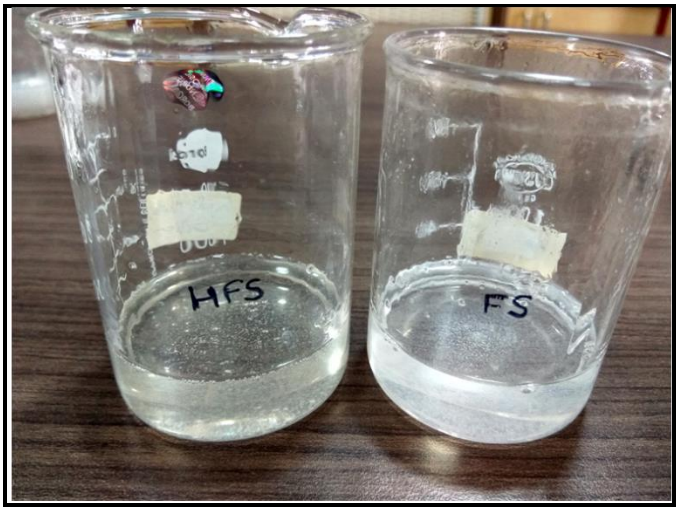


Figure 10.1 STF of a) hydrophobic fumed silica and b) hydrophilic fumed silica dispersed in PPG425

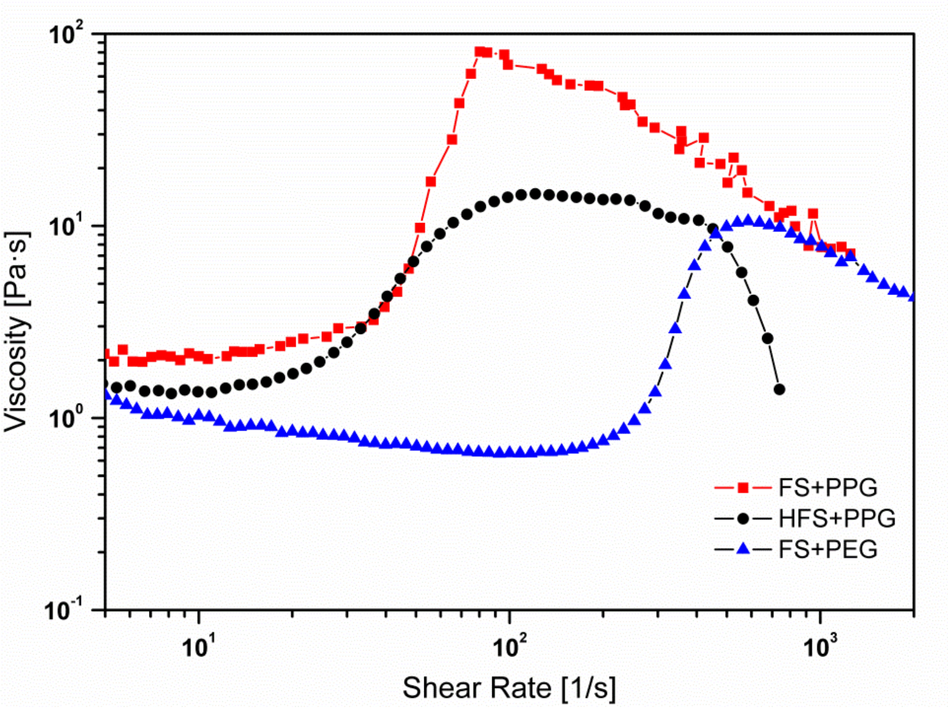
10.3 Results and discussion

The samples prepared by dispersing hydrophobic fumed silica in PEG did not result in STF due to a highly flocculated morphology of hydrophobic silica which confirms that some hydrophilic character of the particle is required for forming STF with PEG which is hydrophilic.

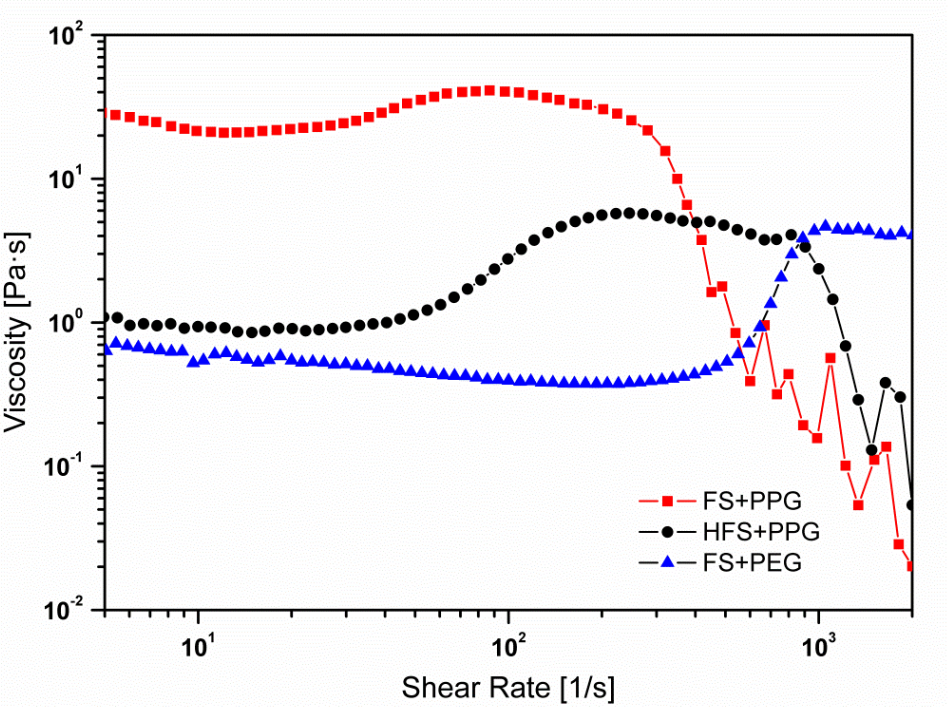
10.3.1 Steady-state rheology

The viscosity versus shear rate plots for three different STF at 25^0C (Figure 10.2) indicate that both initial (3 Pa.s) and critical viscosities (80 Pa.s) of the FS+PPG STF has significantly high. The critical viscosity of HFS+PPG STF and FS+PEG STF is almost same i.e. 16 and 10 Pa.s, respectively with a significantly higher critical shear rate for the latter. Additionally, critical shear rate values are almost the same for both FS+PPG and HFS+PPG i.e 20 s^{-1}, which confirms that critical shear rate values depend on base liquid medium, thus, from this it can be assumed that as PPG has less hydrophobic character, therefore, for HFS+PPG STF very less amount of hydrophobic fumed silica particles will interact with PPG contributing to shear thickening behavior and most of it will cause flocculation. However, for FS+PPG STF most of the hydrophilic fumed silica particles will interact with PPG contributing largely to shear thickening properties, although some fumed silica particles not bonded with PPG will cause initial flocculation resulting in low values of critical shear rate. Moreover, after a week of storage gel-like structure will be formed in both the STF due to flocculation caused by unbounded fumed silica particles. Additionally, for FS+PEG STF, all of the fumed silica particles should interact with PEG molecules preventing both initial and after storage flocculation. Moreover, for this STF a stronger network will be formed contributing to high values of critical viscosity. However, overall values of critical viscosity is less compared to other two STF which would be due to the high molecular weight of PPG used in those STF.

From Figure 10.2b it can be seen that as the temperature increases from 25^0C to 35^0C, critical viscosity decreases by a factor of 2 for all three STF. For FS+PPG, HFS+PPG and FS+PEG STF, critical viscosity values are 40, 6, and 4 Pa.s, respectively. Moreover, for FS+PPG STF shear thickening behavior decreases a lot and highly flocculated morphology can be observed due to a high value of viscosities at low shear rates. However, for HFS+PPG and FS+PEG STF, there is not much change in low shear viscosity values when compared with 25^0C. although, critical viscosity values of these two STF decreases a lot. At 45^0C there is further decrease in critical viscosities and viscosity for all three STF decreases by about 10 times at 55^0C i.e. having very low critical viscosity values of 8 Pa.s for FS+PPG STF and 1 Pa.s for both HFS+PPG and FS+PEG STF (Figure 10.3b). Steady-state profiles of two STF (FS+PPG and HFS+PPG) at low temperatures are shown in Figure 10.4. At 15^0C the critical viscosity values increase by a factor of 2 (Figure 10.4a), however, at 5^0C there is a much larger increase in critical viscosity values of both FS+PPG and HFS+PPG STF which is about 6 times i.e. 500 Pa.s and 100 Pa.s respectively (Figure 10.4b), compared to critical viscosities at 25^0C. Consequently, temperature study shows that the STF containing PPG as a liquid medium are not stable at high temperatures and show flocculated gel-like behavior with shear thinning rheology starting at temperature ≥ 35^0C. However, these STF are stable at low temperatures i.e. 5^0C.

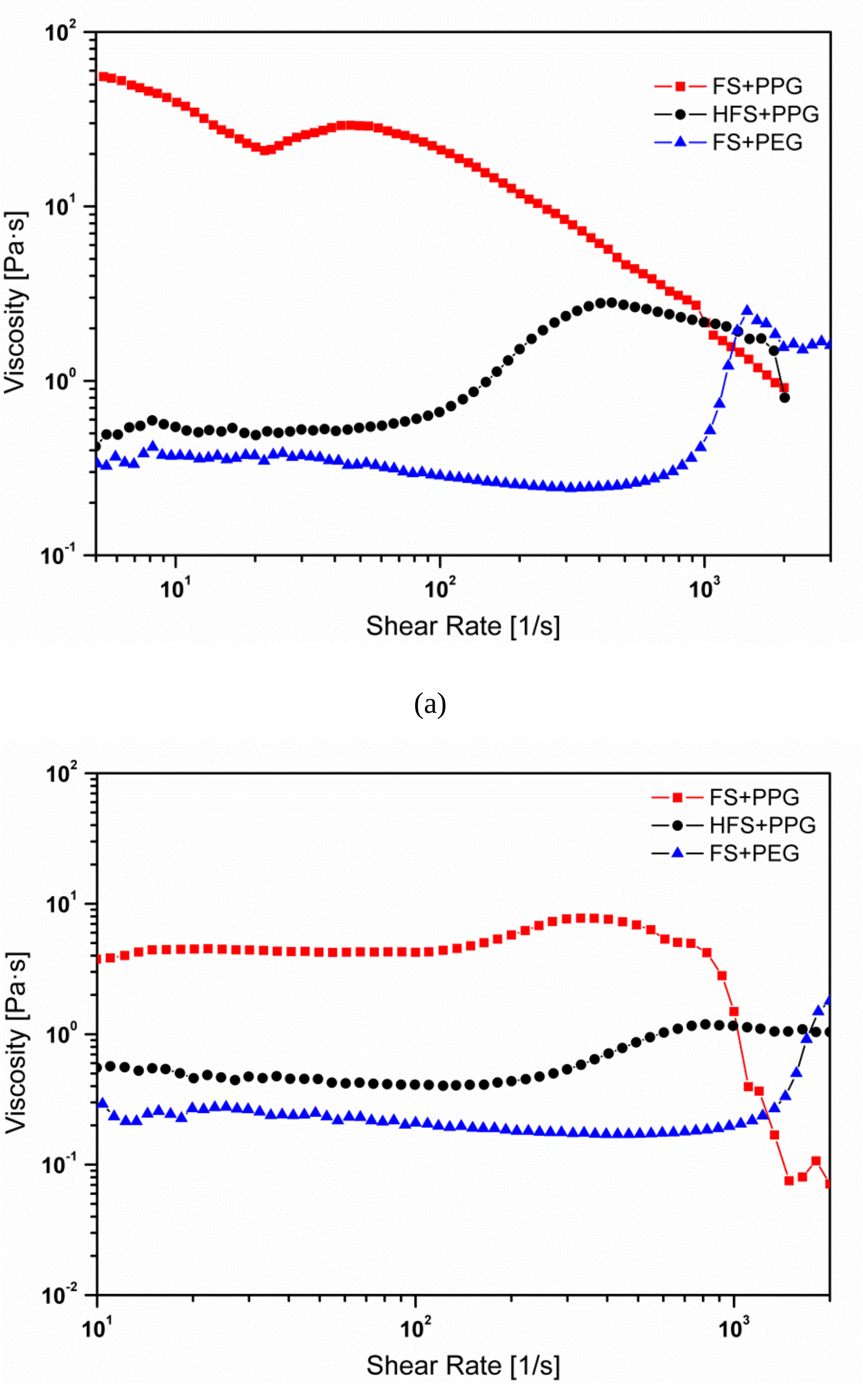


(a)



(b)

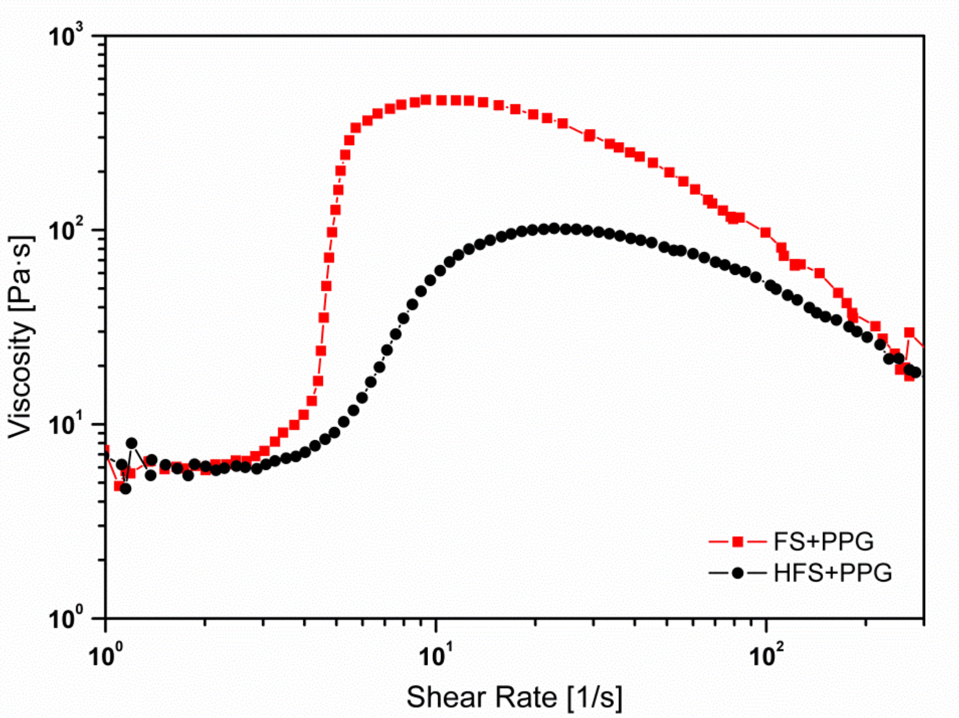
Figure 10.2 Steady-state viscosity profiles a) 25^0C and b) 35^0C



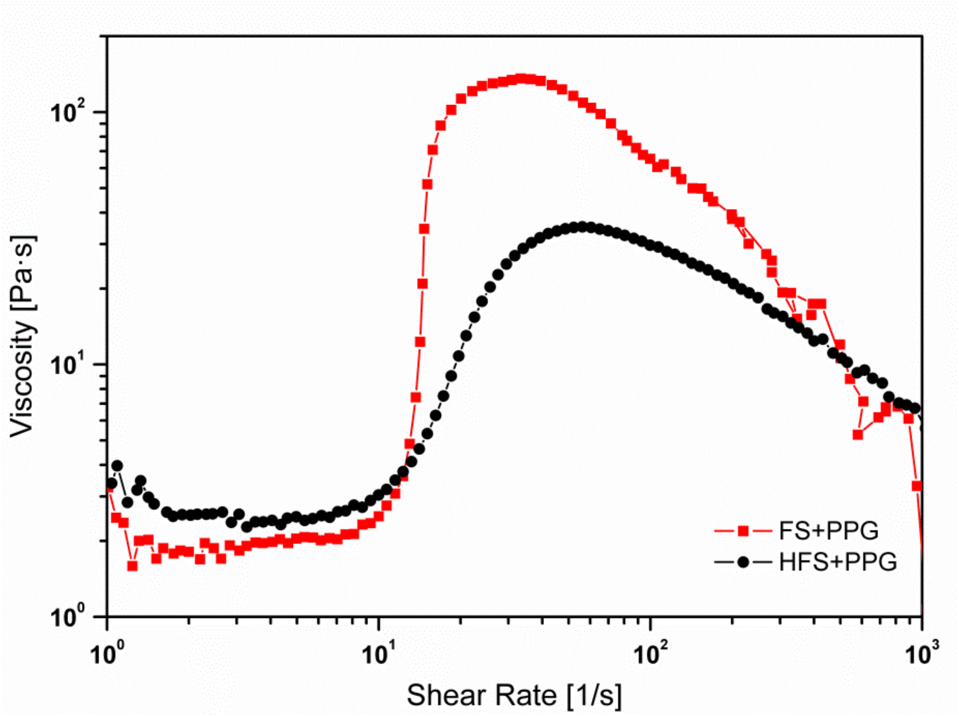
(a)

(b)

Figure 10.3 Steady-state viscosity profiles a) 45^{0}C and b) 55^{0}C



(a)



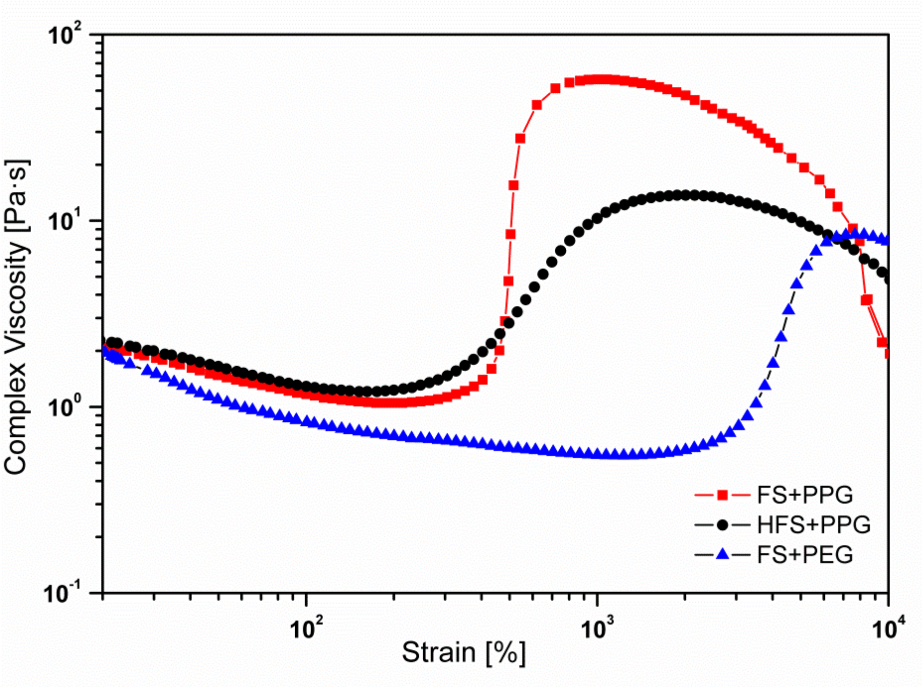
(b)

Figure 10.4 Steady-state viscosity profiles at a) 5^0C and b) 15^0C

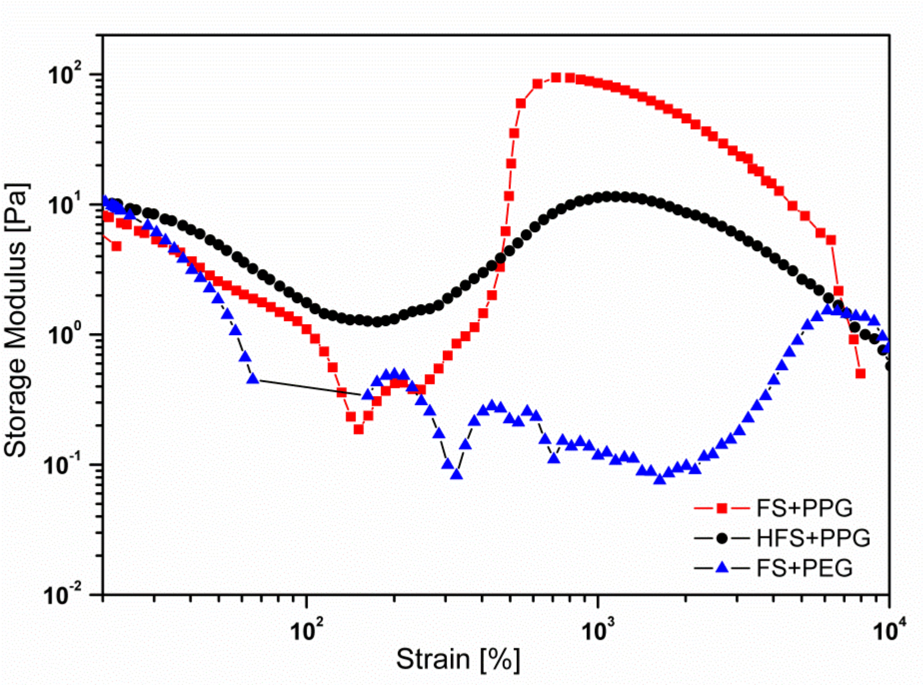
10.3.2 Dynamic-state rheology

Dynamic rheological profiles of all three samples at a constant frequency of 10 rad/s are shown in Figure 10.5, with respect to all three parameters (storage modulus, loss modulus, and complex viscosity).

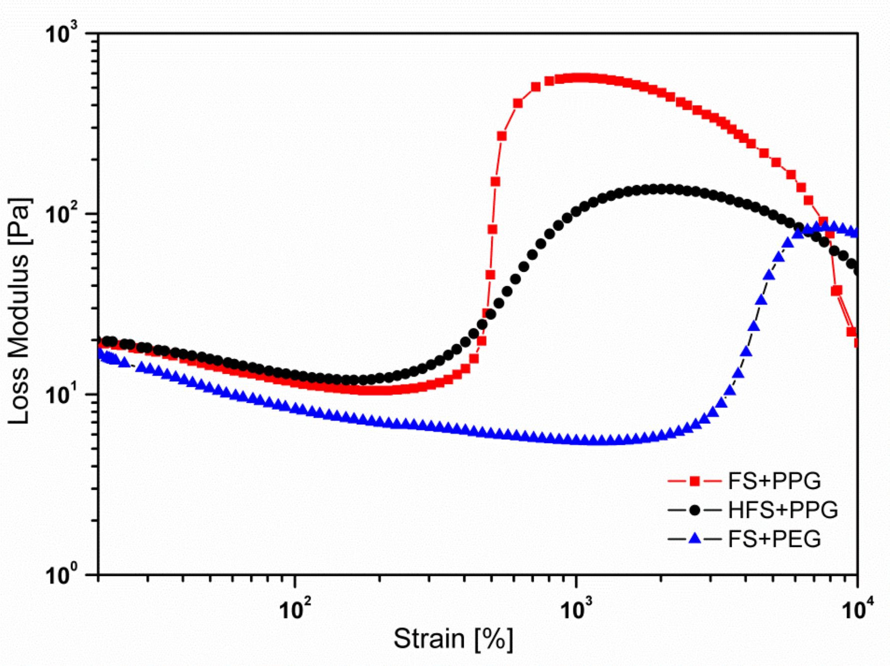
Figure 10.5a again shows a similar behavior to steady-state rheology i.e. a large jump in complex viscosity after a critical strain is observed for in FS+PPG STF and in other cases, the critical value of complex viscosity is almost same. For FS+PPG STF the value of complex viscosity (about 60Pas) is less than that of steady-state viscosity (about 80Pas) whereas HFS+PPG and FS+PEG show similar values of viscosities in both steady state and dynamic rheology. This indicates towards the unstable or more sensitive nature of FS+PPG STF towards the type of flow deformation. Strain hardening is observed at 400% for FS+PPG and HFS+PPG but for FS+PEG strain hardening is at 3000%. Storage modulus value for FS+PEG STF is 1 Pa which is very less compared to FS+PPG and HFS+PPG STF having 100 Pa and 10 Pa respectively. However, the storage modulus values of both FS+PEG and HFS+PPG STF are similar i.e 120 Pa and 80 Pa respectively (Figure 10.5b and c). Although, FS+PPG STF show extremely large values of loss modulus i.e. 600 Pa. Consequently, FS+PPG STF possessed very high viscous and elastic properties compared to all other STF however, FS+PEG STF show less elasticity than HFS+PPG STF but viscous properties for both STF are similar. At constant frequencies of 30 and 70 rad/s profiles are shown in Figures 10.6 and 10.7 respectively.


Complex Viscosity [Pa·s]
10^2
10^1
10^0
10^{-1}
Strain [%]
10^2
10^3
10^4
FS+PPG
HFS+PPG
FS+PEG

(a)


Storage Modulus [Pa]
10^2
10^1
10^0
10^{-1}
10^{-2}
Strain [%]
10^2
10^3
10^4
FS+PPG
HFS+PPG
FS+PEG

(b)

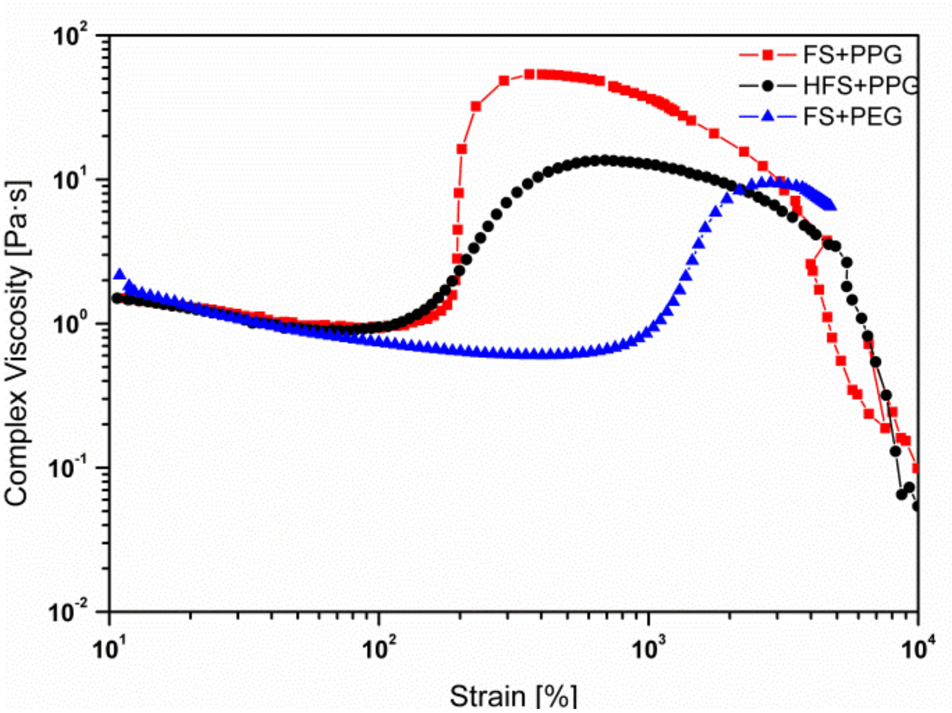


(c)

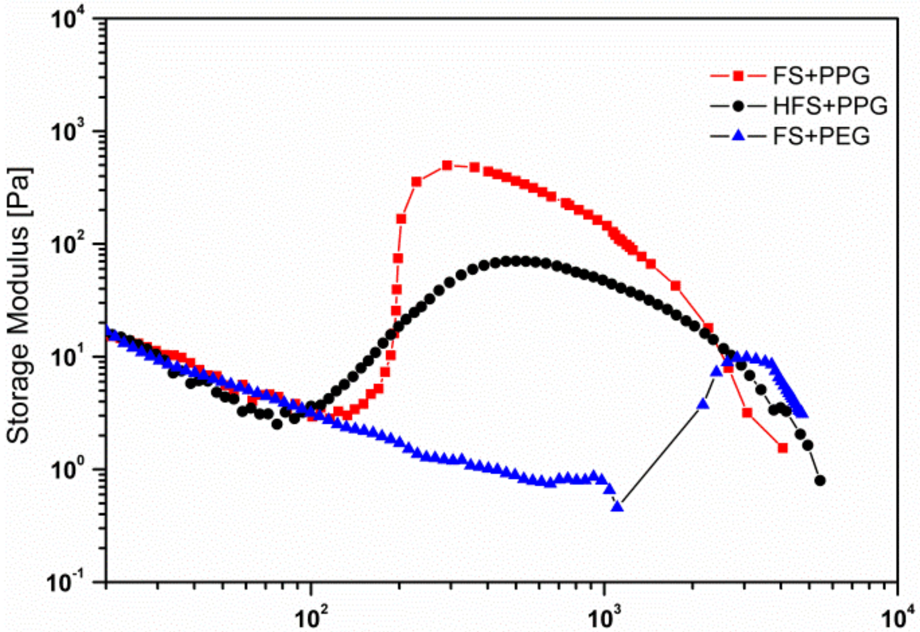
Figure 10.5 Amplitude sweep showing profiles of (a) complex viscosity (b) storage modulus and (c) loss modulus at 10 rad/s

Similar profiles are obtained at 30 rad/s as shown in Figure 10.6 with negligible change in critical values of all three parameters. However critical strain values for all parameters decreases to half. Thus, strain hardening is observed at 200% for both FS+PPG and HFS+PPG but for FS+PEG strain hardening is at 700%.

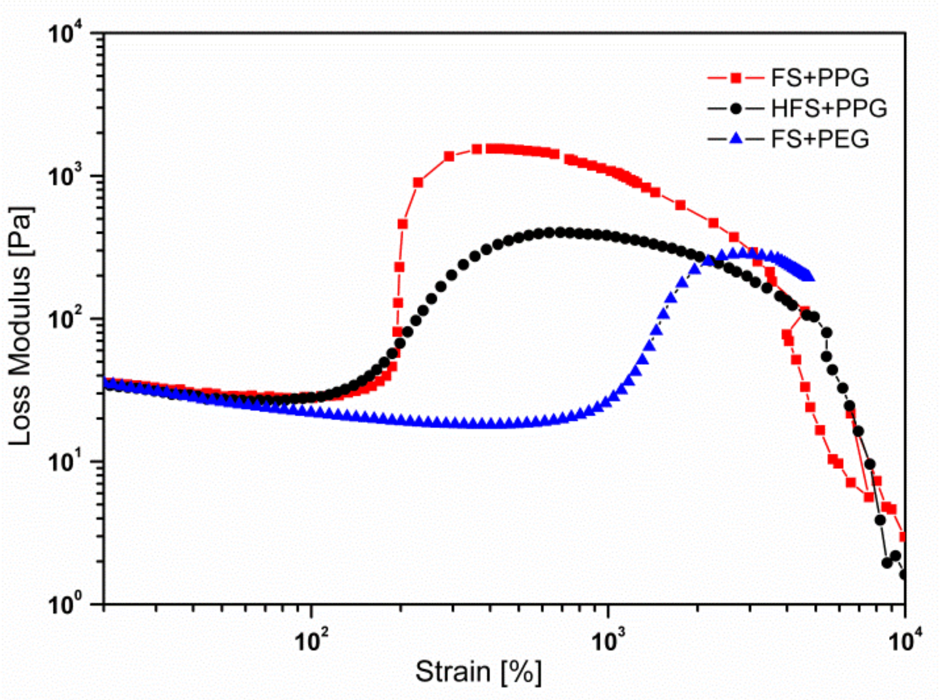
At 70 rad/s, dynamic rheology profiles (Figure 10.7) show a large increase in values of both moduli with an almost negligible change in complex viscosity. Strain hardening is observed at 100% for both FS+PPG and HFS+PPG STF but for FS+PEG strain hardening is at 400%. Frequency sweep of FS+PPG and HFS+PPG STF at constant strain amplitude of 500% for all parameters were shown in Figure 10.8. As frequency increases up to a critical frequency, all parameters increase sharply for both STF. STF of HFS+PPG shows a maximum value of critical viscosity.


FS+PPG
HFS+PPG
FS+PEG
Complex Viscosity [Pa·s]
10^2
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
10^3
10^4
Strain [%]

(a)

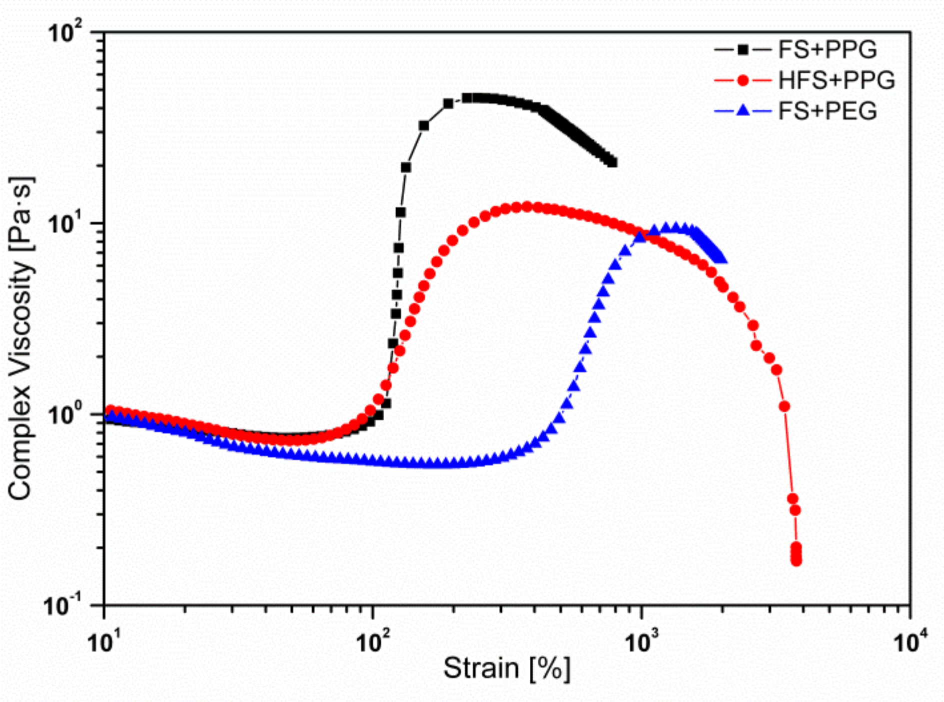

FS+PPG
HFS+PPG
FS+PEG
Storage Modulus [Pa]
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^2
10^3
10^4
Strain [%]

(b)

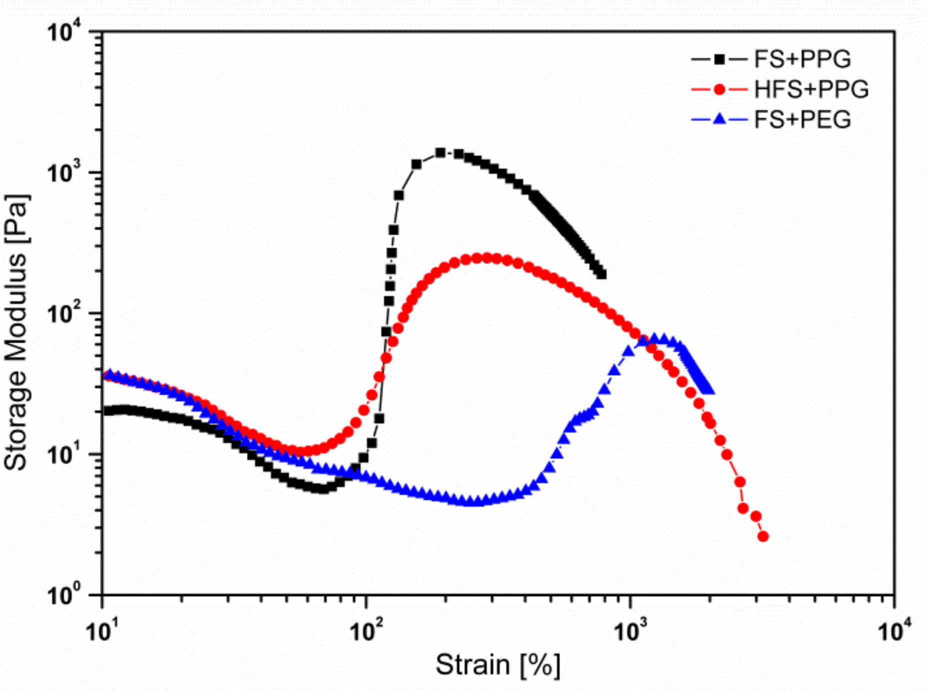


(c)

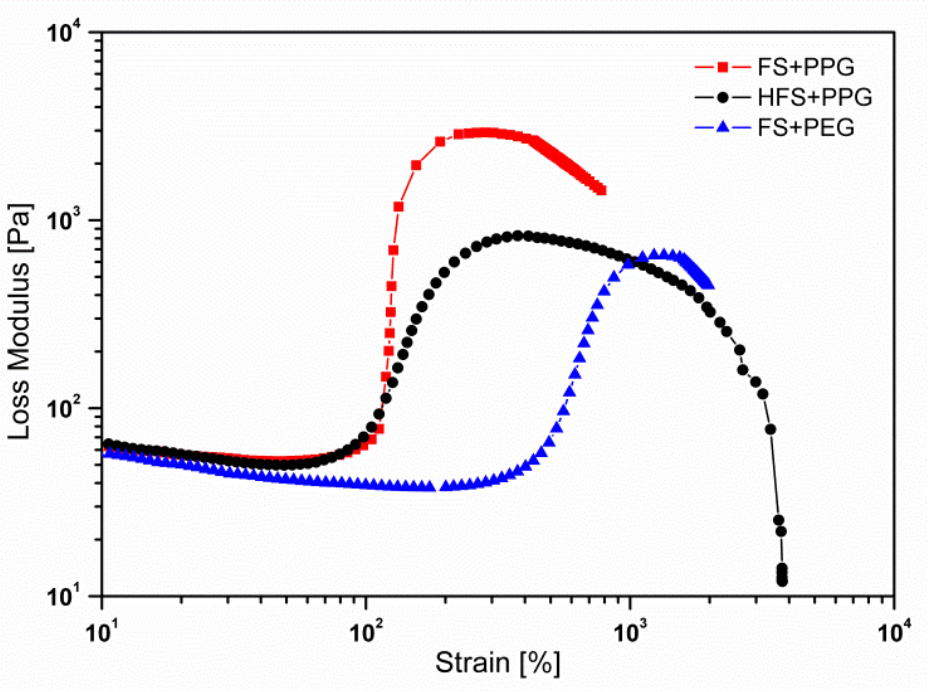
Figure 10.6 Amplitude sweep showing profiles of (a) complex viscosity (b) storage modulus and (c) loss modulus at 30 rad/s



(a)

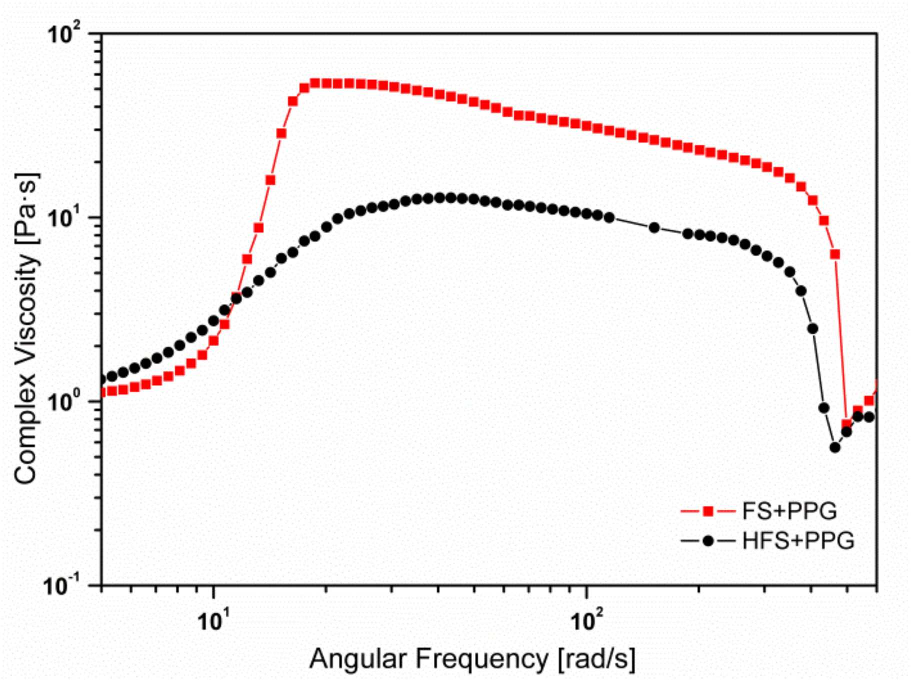


(b)

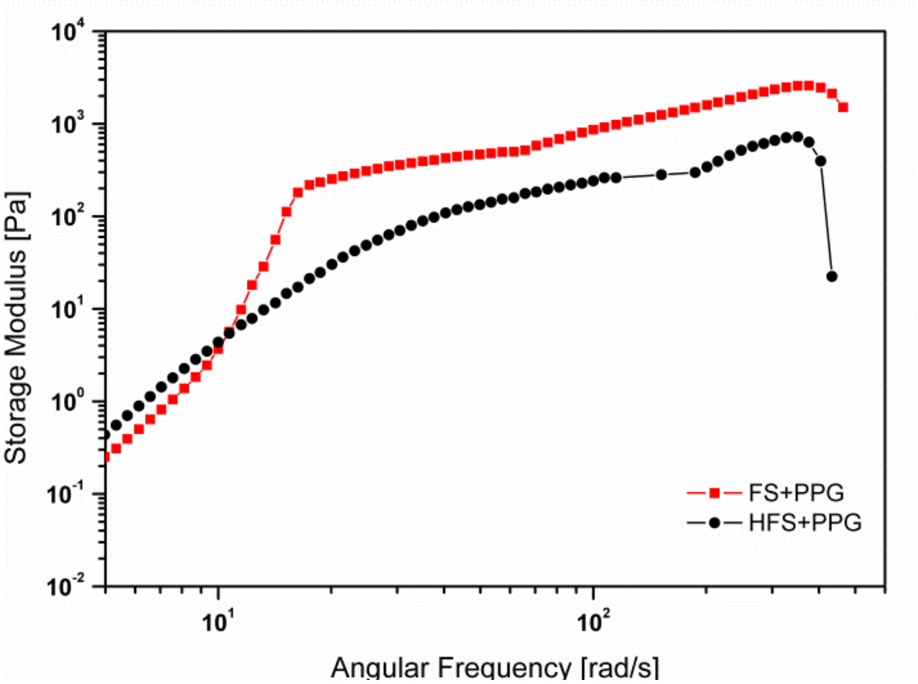


(c)

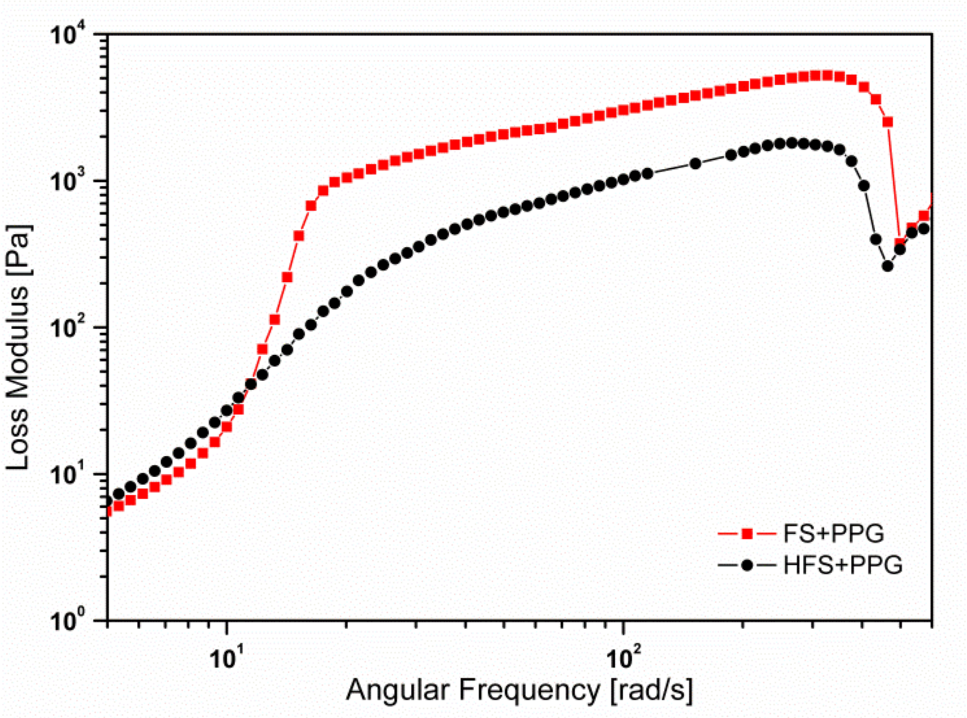
Figure 10.7 Amplitude sweep showing profiles of (a) complex viscosity (b) storage modulus and (c) loss modulus at 70 rad/s


10^2
10^1
10^0
10^-1
Complex Viscosity [Pa·s]
10^1
10^2
Angular Frequency [rad/s]
FS+PPG
HFS+PPG

(a)


10^4
10^3
10^2
10^1
10^0
10^-1
10^-2
Storage Modulus [Pa]
10^1
10^2
Angular Frequency [rad/s]
FS+PPG
HFS+PPG

(b)



(c)

Figure 10.8 Frequency sweep showing profiles of (a) complex viscosity (b) storage modulus and (c) loss modulus at 500%

10.4 Conclusion

The effect of varying material (particle and liquid) properties on the resultant shear thickening effect were quantified and explained with the aim of providing the ability to tailor properties of STF for potential applications. PPG has both hydrophobic and hydrophilic character having more hydrophilicity than hydrophobicity. Consequently, the STF consisting of PPG with hydrophilic fumed silica results in high shear thickening properties than STF with hydrophobic fumed silica. However, both STF having PPG as the liquid medium are not stable on storage due to flocculation or gel-like structure resulting from unbounded hydrophilic and hydrophobic fumed silica. Hydrophobic fumed silica dispersed in hydrophilic or polar PEG results in most stable STF attributed to all of the fumed silica particles interacting with PEG preventing any flocculation.

In dynamic state rheology also FS+PPG STF shows the highest values of all parameters. Although, FS+PEG STF shows lowest elastic properties, however viscous properties of FS+PEG

STF are comparable to HFS+PPG STF with very high critical strain values than HFS+PPG STF. As the value of constant frequency increases, all parameters increase a lot for all three STF.

Therefore, the STF consisting of hydrophobic fumed silica and polypropylene glycol that thickens at very low shear rate would be useful in sensitive applications such as acoustic dampening or low impact situations whilst the STF consisting of hydrophilic fumed silica and polypropylene glycol that thickens at higher shear rate would be optimally used in high impact scenarios such as ballistic impacts.

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Chapter 11 Conclusion and future scope of work

11.1 Conclusion

This research study reports the key rheological findings of STF consisting of fumed silica particles and PEG along with different particles and suspension medium. It has opened new horizons for tailoring the properties of shear thickening fluids having wide applicability along with good stability with respect to time and temperature. The results of the thesis with respect to critical viscosity and critical shear rate are summarized in Table 11.1 to 11.3.

11.1.1 Effect of raw materials and processing conditions on rheology

- Probe sonication technique is most suitable for nano-dispersion of particles in liquid medium.
- Time of sonication is very critical for suspensions to show shear thickening properties and is composition specific.
- 20% fumed silica (11 nm) STF is an optimum concentration for base STF for studying effects of additional fillers.
- Fumed silica (11 nm) is more stable and shows high viscosity and high critical shear rate which are desired from an application point of view as compared to silica (400 nm) STF. Also fumed silica shows shear thickening behavior at much lower loading levels than silica, thus resulting in a lot of potential weight savings.
- Nanoclays can be used only as additives in STF for enhancing properties and proper exfoliation of clay particles is required prior to dispersion of fumed silica particles.

Table 11.1 Comprehensive results of clays as additives at 25^0C

S.No.	Additives	Concentration of additive in 20 % fumed silica–PEG STF	Critical shear rate [1/s]	Critical viscosity[Pa.s]
1	MMT(Not stable)	3 phr	400	12
2		5 phr	200	27
3	Closite®15A	3 phr	100	40
4		5 phr	70	55
5	Kaolin	3 phr	160	25
6		5 phr	50	47
7	Halloysite	3 phr	100	27
8		5 phr	50	52
9	Nanomer	3 phr	115	20
10		5 phr	54	55
11	Alumina	3 phr	200	21
12		5 phr	100	21
13	PEG4600	1 phr	130	51
14		3 phr	30	115
15		5 phr	15	190
16	PEG6000	1 phr	60	90
17		3 phr	10	150
18		5phr	25	227
19	PEG10000	1 phr	90	70
20	(Not stable)	3 phr	100	47
21		5phr	2	252

Table11.2 Comprehensive results of silicone oil of different viscosities as additives at 25^{0}C

S.No.	Additives	Percentage of silicon oil in 20 % fumed silica – PEG STF	Critical shear rate [1/s]	Critical viscosity [Pa.s]
1	100 cst silicone oil	10 %	180	15
2		15 %	70	25
3	500 cst silicone oil	10 %	50	52
4		15 %	23	125
5	1000 cst silicone oil	10 %	30	62.5
6		15 %	10	190

Table 11.3 Comprehensive results of different fumed silica as additives at 25^{0}C

S.No.	Composition	Critical shear rate [1/s]	Critical viscosity [Pa.s]
1	Fumed silica (hydrophilic)-PPG475 (stable for about 3 days)	100	80
2	Fumed silica (hydrophobic)-PPG475	100	10
3	Fumed silica (hydrophilic)-PEG200	250	10

11.1.2 Nanoclays of different chemical and physical properties as additives: increase in hydrodynamic forces (Table 11.1)

- 5 phr is the maximum concentration of nanoclays that can be used as additives for 20% fumed silica STF.
- Additives did not affect the low shear rate and low strain profiles i.e. viscosity of STF remains low on addition of clays. However, high shear rates or high strain results in enhanced shear thickening behavior as the clay increases the hydrodynamic forces, which came to play only after critical shear rate and strain is achieved.
- Non-swelling clays (Kaolin and Halloysite) shows large shear thickening properties at, both low and high temperatures compared to swelling clays (MMT and Closite®15A), which can form gels at an even small concentration resulting in overall shear thinning behavior.
- Rod-shaped (Halloysite) clays increase critical viscosity more than layered (Kaolin) clays.
- Ionic modified clay as additive results in an increase in elastic nature of STF.
- Dynamic-state rheology is not much affected by the shape of clay particles.
- Clay as additives results in a very large difference in values of viscous and elastic modulus.

11.1.3 Effect of nanomer clay as an additive (Table 11.1)

- Nanomer clay as nano-additive make STF easy to process, more stable under both steady and dynamic deformations as well as temperature variations compared to fumed silica STF.
- Although, the 5 phr concentration of nanomer clay as additive show very low values of critical viscosity compared to fumed silica as additives, however, elastic and viscous properties of STF containing nanomer clay are comparable to that of the STF with the same amount of fumed silica as additives.

11.1.4 Effect of alumina particles as an additive in 20% fumed silica-PEG STF (Table 11.1)

- Increase in concentration of alumina particles did not increase critical viscosity but critical shear rate decreases.

- The 3 phr concentration of alumina particle is optimum and shows high critical viscosity values to that of same concentration of MMT clay but comparable to that of nanomer clay as additives. However, compared to nanomer clay it shows high critical shear rate values.

- Interestingly, alumina particles as additives show high values of both the moduli as compared to MMT clay, may be due to high plasticity of the clay which makes STF soft under high strains.

11.1.5 Polyethylene glycol of different molecular weights as additives: increase in depletion forces (Table 11.1)

- The STF comprising of different molecular weight PEG as additives demonstrate noticeable shear thickening behavior for molecular weight of 6000 where the critical viscosity of 5 phr concentration is about 5 times more when compared with the same concentration of Closite®15A clay as additives however critical shear rate decrease about by 5 times.
- PEGs as additives also show high values of both moduli with not much difference in the values of storage and loss modulus in contrast to behavior shown by clay as additives.
- With respect to shear thickening properties and easy in processing, the optimum molecular weight of PEG was found to be 6000.
- There is a large decrease in shear thickening properties with increase in temperature for PEGs as additives, in contrast to the behavior shown by clays.
- PEGs of high molecular weight, under some limitations can be used as additives for increasing shear thickening behavior due to their molecular structure and capability of forming bridges.

11.1.6 Effect of silicone oil compounded PEG as suspension medium (Table 11.2)

- STF of nano-fumed silica dispersed in PEG-silicone oil exhibit a high shear thickening response.

- 100cst silicone oil can be used to add up to 20% concentration of PEG200, whereas for both 500cst and 1000cst silicone oil maximum concentration that can be added is 15% because of highly viscous nature of the composite suspension medium.
- 15% is an optimum concentration after which increase in concentration does not result in an increase in moduli.
- At high concentrations, silicone oil shows more elastic nature, however, viscous nature do not change much.
- 500cst silicone oil is more stable than 1000cst both at high and low temperatures.

11.1.7 Effect of hydrophilicity (Table 11.3)

- Some hydrophilic character of the particles is required to form STF with PEG.
- PPG, which is a semi-polar liquid, as dispersion medium makes STF unstable under dynamic shear as well as under low and high temperatures due to unbounded hydrophobic and hydrophilic fumed silica particles resulting in flocculation and gel behavior.
- Elastic nature of STF depends more on the molecular weight and viscosity of the liquid medium as hydrophilic fumed silica STF with PPG showed high elasticity compared to PEG.

11.2 Future scope of work

- ➢ Armed with knowing the exact effect of particles, particle shapes and size, functionality, temperature, dispersion medium etc. on the STF behavior, better STF can be tailor designed as per the requirements of existing or future applications.
- ➢ STF impregnated Polyurethane foams can be synthesized/processed for better impact resistance.

LIST OF PUBLICATIONS

The results incorporated in the thesis are fully documented. The following publications in SCI journals have come out of the work carried out. Some of the work has also been presented at national/international conferences/seminars.

1. International SCI Journals

1.1 Publications Related to Ph.D. Work

- Effect of addition of different nano-clays on the fumed silica-polyethylene glycol based shear-thickening fluids ; **Mansi Singh,** Rajeev Mehta, Sanjeev K Verma and Ipsita Biswas; Materials Research Express ; DOI: 10.1088/2053-1591/aa9f3f **(IF: 1.449)**

- Effect of molecular weight of polyethylene glycol on the rheological properties of fumed silica-polyethylene glycol shear thickening fluid; **Mansi Singh,** Sanjeev K Verma, Ipsita Biswas and Rajeev Mehta; Material Research Express, DOI: 10.1088/2053-1591/aac25c/meta **(IF: 1.449)**

- Effect of addition of silicone oil on the rheology of fumed silica and polyethylene glycol shear thickening suspension; **Mansi Singh,** Sanjeev K Verma, Ipsita Biswas and Rajeev Mehta; Journal of Polymer Engineering; DOI: https://doi.org/10.1515/polyeng-2018-0054 **(IF: 1.072)**

- Rheology of Fumed Silica and Polyethylene Glycol Shear Thickening Suspension with Nanoclay as an Additive; **Mansi Singh** , Sanjeev K Verma, Ipsita Biswas and Rajeev Mehta; Defence Science Journal; DOI: https://doi.org/10.14429/dsj.69.12420 **(IF: 0.589)**

1.2 Other Publications in the Related Area

- Steady shear and dynamic strain thickening of halloysite nanotubes and fumed silica shear thickening composite, Pavni Passey, **Mansi Singh**, Sanjeev K. Verma, Debarati Bhattacharya and Rajeev Mehta; Journal of Polymer Engineering, DOI: https://doi.org/10.1515/polyeng-2018-0043 **(IF: 1.072)**

1.3 Under Review/ Communicated

- Effect of interaction between dispersed particles and dispersion medium on the rheology and stability of shear-thickening fluids, **Mansi Singh** and Rajeev Mehta; Smart Materials and Structures, Article reference: SMS-107633. **(IF: 3.543)**

- Rheological testing protocol for bi-dispersed shear thickening fluids, Pavni Passey, **Mansi Singh**, Sanjeev K. Verma, Ipsita Biswas and Rajeev Mehta; Journal of Macromolecular Science, Part B (Submission ID: 189670689) **(IF: 0.778)**

1.4 In preparation

- Effect of carrier fluid on the rheology and stability of shear thickening fluid ; **Mansi Singh Rajeev** Mehta

2. Conference proceedings

- Mansi Singh and R.Mehta, “Shear - Thickening Fluids: Processing, Rheology And Their Applications” International Conference on Advances in Polymer Science & Technology (APA-2017) held at 23-25 November, 2017 Radisson Blu Hotel, Dwarka, New Delhi, India.
- Award given to team for the “Best Innovative Young Researcher” at the 4th International Conference on Nanoscience and Nanotechnology (ICONN 2017) at SRM University. The conference was held during 9-11 August 2017
- Mansi Singh and R.Mehta, Short Invited Lecture category -Study Of Dynamic Rheology And Effect Of Temperature on bidisperse shear thickening fluid ‘Highly correlated systems (IMHCS-2017)’ held at Mahatma Gandhi University (MGU) on March 24-26, 2017.

- R.Mehta and Mansi Singh, 3rd international conference on Nanostructured Materials and Nanocomposites (ICNM 2015), Hindustan College of Science and Technology, Mathura, 12-14 December 2015.
- Mansi Singh and R.Mehta, Shear thickening fluids and their applications, INDO-UK Workshop on Sustainable Polymer Application (IUWSPA 2015), Thapar University, 8-9 Dec,2015.

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PAPER

Effect of addition of different nano-clays on the fumed silica-polyethylene glycol based shear-thickening fluids

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Keywords: shear thickening fluid, viscoelasticity, rheology, fumed silica, clay

Supplementary material for this article is available online

Abstract

A comparative study of the rheology of shear thickening suspensions of 20% fumed silica in polyethylene glycol (PEG200) with different nano clays as additives has been done. The nano-clays used are montmorillonite (MMT), Closite15A, Kaolin and Halloysite clay. The objective was to study the effect of relatively cost-effective clays as a partial substitute of silica. Specifically, the effect of type, concentration, temperature and frequency were considered. The results indicate that the shear thickening properties of Closite15A as additive in temperature ranges of 25 °C–45 °C performs the best and Halloysite performs best at higher (55 °C) and lower temperatures (5, 15 °C). The elasticity effects in dynamic experiments were markedly enhanced by Halloysite clay addition. Addition of MMT, however, led to insignificant enhancement in critical viscosity in steady-state as well as dynamic state-rheology. Interestingly, shear thickening fluid (STF) with all clay except MMT was stable after storing for more than a month. These findings indicate that the introduction of nano-clay as additives is a promising and cost effective method for enhancing the STF behavior which can be utilized in high impact resistant (about 3000% strain and 300 rad s^{-1} frequency) applications.

1. Introduction

Shear thickening fluids (STF) are non-Newtonion and stabilized colloidal suspensions of rigid nanoparticles in a polymeric medium that exhibit a significant and discontinuous increase in viscosity when the applied stress is increased [1–4]. STF impregnation of protective materials provide a suitable approach in strengthening these materials by providing benefits to fibers like Kevlar and Twaron without compromising the inherent light weight or flexibility of these fabrics [5, 6]. More stringent demands and new applications in body armor and damping devices drive towards the development of specialty STF, with a relatively high shear thickening properties with a relatively low concentration and weight. Additive modification of existing STF provides an elegant route towards STF with new properties [7–9]. Traditionally, the system consists of large quantities of spherical silica microparticles (>60 vol%) dispersed in polymer like polyethylene glycol but for nanoparticles like fumed silica dramatic changes in properties are possible at very low loadings (>18 vol%) [10, 11].

Clay particles are known to increase the material strength of many composites. A concentration of <10 wt% of clay can be fully exfoliated for improved properties in polymer nanocomposite [12]. Also, Kaolin clay naturally has been shown to exhibit some shear thickening properties [13]. Montmorillonite is a naturally occurring smectite clay mineral. It has swelling quality i.e. can take up extra water in their interlayers. Depending on surface modification of the clay layers, montmorillonite can be dispersed in a polymer matrix to form polymer-clay nanocomposite. A popular and relatively easy method of modifying the clay surface, making it more compatible with the organic matrix, is ion exchanging. The cations are not strongly bound to the clay surface so small molecule cations can replace the cations present on the clay [14]. By exchanging it with various organic cations (e.g. quaternary ammonium ions with long alkyl chains as in Closite15A), MMT can be

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PAPER

Effect of molecular weight of polyethylene glycol on the rheological properties of fumed silica-polyethylene glycol shear thickening fluid

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Abstract

The steady-shear viscosity and dynamic visco-elastic behavior of suspensions of 20 wt% fumed silica-polyethylene glycol (PEG200) shear thickening fluid (STF) with different concentrations of various molecular weight PEG (4600, 6000 and 10000) has been studied. The results demonstrate that with an increase in the molecular weight of dispersing medium, the shear thickening parameters are significantly enhanced. In steady-state rheology, addition of PEG6000 as an additive results in high shear thickening at both low and high temperatures whereas in dynamic state, PEG4600 gives high values of all dynamic parameters. Additionally, long polymer can interconnect several particles, acting as cross-links which explain the mechanism of the enhancement in viscosity. Interestingly, compositions having PEG10000 as additive exhibits shear thinning rheology. Long polymer chains increases hydrodynamic forces thus aggregation of particles increases. Also, the results demonstrate the effect of high molecular weight PEGs on the elasticity and stability of the STF, which is important with regard to high impact resisting applications.

1. Introduction

STF belongs to the category of smart materials along with magnetorheological and electrorheological fluids [1, 2]. Similar to magnetorheological fluid which consists of magnetic particles suspended in a carrier fluid, STF is a suspension of hard inorganic particles dispersed in a polymeric fluid. Shear thickening fluids (STF) show a dilatant and a non-Newtonian fluid behavior. When subjected to an impact, after a critical shear rate STF suddenly exhibits a reversible and discontinuous increase in viscosity [3, 4]. Thus, STF can be exploited in the design of damping and control devices including seismic protectors for buildings and shock absorbers for sports equipment, clutches, brakes etc due to its self-limiting maximum rate of flow [5–9]. There has been a lot of interest in using STF in liquid body armor by impregnating high performance aramid fabrics such as Kevlar with STF [10–17]. The impregnated body armor could provide rigidity for resisting piercing by bullets, stabbing knife blows, and similar attacks yet allowing the flexibility and reduced weight to the wearer. STF are composed of dispersions of rigid particles of nano or micron range dimensions, in a carrier fluid. Various researchers have widely used single solid and liquid phases, specifically silica dispersions in polyethylene glycol (PEG) for making STF for various applications [11, 18]. The accepted mechanism of shear-thickening is the hydrocluster mechanism in which initially, the hydrogen bonds are formed between polymer chains and particles, and under high shear, formation of hydro-clusters takes place [19, 20]. Many studies over the last several decades have focused on the factors that impact the rheological properties of STF, most dominating being the dispersed particle and dispersion medium properties [21–23]. Suspensions can be designed with different particles and solvents to produce various useful material properties [24]. Our earlier results showed that for tailoring the shear thickening properties i.e. critical shear rate (shear rate after which shear thickening starts) and critical viscosity (peak value of viscosity), different additives like different nano-clays of high aspect ratio can be used [25].

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Effect of addition of silicone oil on the rheology of fumed silica and polyethylene glycol shear thickening suspension

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Abstract: Shear thickening fluids (STF) are stabilized and concentrated colloidal suspensions of hard nanoparticles in a liquid medium (polymer) that, under the influence of impact forces, show non-Newtonian fluid behavior (shear thickening) dissipating the energy of impact. The viscosity of the dispersion medium should be optimum to lead to an increase in shear thickening, and at the same time, should also allow proper dispersion of the particles. Herein, an STF based on 20 wt% fractal nano-fumed silica particles of 11 nm suspended in a liquid medium of polyethylene glycol (PEG 200) with different concentrations of silicone oil was prepared. These systems were studied in terms of steady-state and dynamic-state rheological behavior under a wide range of temperature, shear rate, strain rate and frequency. The STF with replacement of up to only 20% of PEG with silicone oil as the liquid medium shows a large increase (about four times) in shear thickening parameters when compared with STF containing only PEG under the same processing conditions. It also shows more elastic behavior at high frequencies which are due to the high cross-linking property of silicone oil, contributing to much-improved properties, which are highly desirable from the view point of many applications.

Keywords: fumed silica; rheology; shear thickening fluids; silicone oil; viscoelasticity.

1 Introduction

Shear thickening fluids (STF) nowadays have become one of the most preferred choices of engineers and scientists, due to their high resistance to impact energy [1–5]. The STF can be exploited in the design of damping and control devices including seismic protectors for buildings and shock absorbers for sports equipment, clutches, brakes, etc. due to its self-limiting maximum rate of flow [6–10]. There is a tremendous effort going on by various researchers to impregnate high-performance aramid fabrics, such as Kevlar, with STF for liquid body armor [8, 11–15]. This impregnated body armor could provide rigidity for resisting piercing by bullets, stabbing knife blows, and similar attacks, yet allowing flexibility and relative weightlessness to the wearer [16, 17]. Initially, an STF has very low viscosity at low shear rates and then as the shear rate increases, after a critical shear rate it suddenly exhibits a reversible and discontinuous increase in viscosity or semi-solid like behavior. During shear thickening, it dissipates energy [4, 18]. The shear rheology of an STF is the result of a non-equilibrium microstructure (hydrocluster) under flow due to an outbalance between hydrodynamic (dissipative) and thermodynamic (conservative) forces [7, 19]. Various researchers have widely used silica dispersions in polyethylene glycol (PEG) for making STF for various applications [20–23]. Chain aggregates of nano-particles of fumed silica present a strong ability of structural recovery under shear [24, 25]. PEG is a synthetic polymer which is thermally stable, non-toxic and easily available in bulk quantities [26, 27]. In addition, PEG chains have a strong affinity of adsorption on to the surface of silica nanoparticles through hydrogen bonding. However, PEG has a disadvantage of very low viscosity, rendering a decrease in the overall viscosity of STF [28]. Moreover, the main drawback of traditional silica STF is its low shear strength; indeed, a large volume of silica (>60%) is required for the desired shear thickening properties, which also contributes to the higher weight of the body armor.

Thus, to tailor the shear thickening properties (critical shear rate and viscosity) for body armor applications,

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Rheology of Fumed Silica and Polyethylene Glycol Shear Thickening Suspension with Nano-clay as an Additive

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ABSTRACT

Shear thickening properties of fumed silica-polyethylene glycol (PEG) with shear thickening fluid (STF) of different concentrations and with an organically modified clay, Nanomer I.28 E as nano-additive have been investigated by both steady-state and dynamic state rheology. Difference in rheology if instead of nanoclay, an equal wt% of additional fumed silica is added to 20 per cent fumed silica-PEG200 STF, has been studied. At 25 °C, in case of addition of nanoclay the increase in critical viscosity is less than that observed for same additional amount of fumed silica. Interestingly, an opposite result is seen at higher temperatures i.e. 45 °C and 55 °C. Moreover, the difference in steady-state and dynamic state viscosity values decreases on addition of nanoclay. It is noted that an increase in concentration of clay increases the value of dynamic parameters whereas for STF of only fumed silica particles the values are constant irrespective of the change in concentration. More importantly, ease of processing, elasticity, stability and consistency of rheological results of STF increases to a significant extent on addition of relatively inexpensive nano-additive.

Keywords: Shear thickening fluids; Rheology; Viscoelasticity

1. INTRODUCTION

Shear thickening fluids (STF) constitutes a subgroup of smart fluids, which shows a dilatant, non-Newtonian fluid behaviour. When subjected to an impact, say of a high velocity projectile, these materials exhibit a reversible and discontinuous increase in viscosity[1-3]. STF are composed of dispersions of rigid particles of nano or micron range dimensions in a carrier fluid which is mostly a polymer[4-6]. Energy absorption, energy dissipation and energy channeling capabilities of these fluids make them suitable for various protective applications in industry, biomedical, and military etc[6-8]. There has been a lot of research on high performance aramid fabrics such as Kevlar impregnated with STF[9-11]. Such a system as body armour can provide rigidity and stiffness to resist high speed projectiles like bullets, knife blows, and other similar attacks yet allowing the flexibility and reduced weight to the wearer. Similarly, research is also going on for STF integration with extra-vehicular activity (EVA) suit for protection against micrometeoroids and orbital debris (MMOD)[12].

The steady-state rheological characteristics of STF in terms of important parameters like critical viscosity (maximum viscosity) and critical shear rate (shear rate at the transition) and the dynamic state properties under oscillatory shear in terms of loss modulus, storage modulus, and complex viscosity as a function of frequency and strain have been reported in literature[13,14]. Among the parameters affecting the shear-thickening behaviour, shape of the particles has been one of the major contributing parameter with rod and plate like particles showing greater critical viscosity than grains and spheres[15-19]. Petel[20], *et al.* suggested that STF consisting of only spherical silica is not optimum for ballistic applications given its low mechanical and thermal properties. Jogun & Zukoski[21] have shown that for clay particles having large aspect-ratio, the excluded volume is much larger than its actual volume and more than that of micron-sized spherical particles[5]. As a result, for the two phase dispersion system of clay as nano-additive in fumed silica-PEG STF the particle motion in the STF will be restricted at much lower volume fraction than the maximum packing fraction of the particles. This is important as it lowers both the cost and weight of the STF. Additionally, the addition of clay particles can increase dispersibility of nanoparticles in the suspension by enhancing the interaction among the particles and resulting in a better clustering of particles. Moreover, fumed silica nano-particles (11 nm - 14 nm) can exhibit very high intensity shear thickening compared to those of simple silica (100 nm - 600 nm) suspensions and that too at much lower loadings (minimum 18 per cent weight fraction)[8,22,23]. The motivation in the present study is to study the rheology of suspensions containing fractal fumed silica particles and high aspect ratio nano-scale clay as additive.

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