



**RHEOLOGICAL CHARACTERISATION OF WATER BASED PAINT USING
ASSOCIATIVE RHEOLOGY MODIFIERS**

By

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A handwritten signature in black ink, appearing to read 'Manasse', enclosed within a hand-drawn oval shape.

ABSTRACT

Water-based paints often suffer defects such as storage instabilities, sagging, poor flow and levelling. The performance of paint rheological additives in the presence of acrylic binders used in the formulation of water-based paints, is not well understood. This study utilises the principles of Rheology to investigate the performance of Hydrophobically Modified Ethoxylated Urethane (HEUR) and Hydrophobically Modified Alkali Swellable Emulsions (HASE) rheology modifiers, in the presence of styrene and pure binders in a decorative water-based paint formulation.

The performance of HASE and HEUR at concentrations ranging from 0 to 1.2 percent was studied in the presence of pure acrylic and styrene acrylic binders. A total of 12 experimental paint samples were prepared and subjected to rheological testing. The rheological tests employed in this study include flow curves, dynamic amplitude sweep, frequency sweep and three interval thixotropy tests (3ITT). The data obtained was then correlated to paint properties such as storage stability, ease of application, levelling and sagging.

HASE was found to have higher thickening efficiency and imparted higher elasticity to paint in the presence of pure acrylic rather than styrene binders. The viscosity curves results showed that paint samples containing HASE have higher viscosities than HEUR, at any given shear rate and irrespective of the type of Binder. The increase in HASE concentration resulted in an increase of paint viscosity throughout the shear rate range; whereas higher HEUR concentration resulted in decrease of paint viscosity in the low shear rate, while high shear viscosity was observed to increase. This finding suggests that higher HEUR concentration can negatively affect the storage stability of water-based paint. Results from the Amplitude sweep test revealed that paints containing HASE have higher storage moduli (G') than HEUR in the linear viscoelasticity region. The fact that HASE produces higher viscosity and higher G' values in the linear viscoelastic region (LVER) suggests that paints thickened with HASE possess good storage stability and are not likely to sag after application. It was also established that the higher elasticity and higher viscosity values at the high shear rate of HASE thickened paints can negatively affect the application and post application properties of paint. On the other hand, the low viscosity values at the high shear rates and lower critical strains obtained for paints containing HEUR suggest that these paints can easily be applied and will have an adequate levelling after application. Paint samples containing HASE are expected to produce a larger film thickness during application, as they have high viscosities at high shear rates and larger storage modulus (G'). Results from 3ITT, flow curve and frequency sweeps revealed that paints made of HEUR containing HEUR will have better flow and levelling properties after their application.

The Power Law, Bingham, Casson and Herschel-Bulkley models were used to fit the viscosity curve test results. Power law and Herschel-Bulkley were found to be the best models as they generated smaller values of RMSE, as well as larger adjusted R^2 and R^2 , respectively.

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DEDICATION

I dedicate this thesis to my loving parents Mr. Albert Cibangwa and Mrs. Julienne Barhasima Cibangwa for their many sacrifices, endless support and encouragement.

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LIST OF SYMBOLS

Symbols	Description	Units
γ	Shear strain	
$\dot{\gamma}$	Shear rate	s^{-1}
δ	Phase angle	
η	Shear viscosity	Pa.s
η_p	Plastic viscosity	
η_c	Casson viscosity	
ρ	Density	Kg/m^3
σ_g	Gravitational Stress	Pa
σ	Shear stress	Nm^{-2}
σ_0	Yield stress	
A	Area of shear face	m^2
F	Force	N
G	Shear modulus	Pa
G'	Storage modulus	Pa
G''	Loss modulus	Pa
K	Consistency parameter	
g	Gravitational acceleration	ms^{-2}
h	Height	M
n	Power law exponent	
v	Velocity	m/s

ABBREVIATIONS AND ACRONYMES

ASE	Alkali Soluble Emulsion
EA	Ethyl Acrylate
FOG	Fineness of Grind
HASE	Hydrophobically Modified Alkali Swellable Emulsions
HEUR	Hydrophobically Modified Ethoxylated Urethane
HEC	Hydroxyethyl Cellulose
KU	Krebs Units
LVER	Linear viscoelastic range
MAA	Methyl acrylic acid
MFFT	Minimum film formation temperature
PA	Pure acrylic
PEG	Polyethylene glycol
SA	Styrene acrylic
SSE	Sum of Square Errors
VOC	Volatile Organic Compounds
R^2	Coefficient of Determination
R_{adj}^2	Adjusted R^2
RMSE	Root Mean Square Root
3ITT	Three Interval Thixotropy Test

CHAPTER ONE

INTRODUCTION

1.1. Background

Water based paint is made of pigments, polymeric binder, solvent and properties enhancing additives (Tiarks et al., 2003; Mariz et al., 2010; Alua, 2012). Water based paints are usually complex fluids and it has been found that rheology can be used as a tool to study and characterise their flow behaviours (Mezger, 2006). Rheology is the study of deformation and flow of matter (Mezger, 2014). Key paint properties such as ease of brushing/rolling, good levelling, opacity, spatter resistance, sag resistance and storage stability; depend mostly on the paint's rheological characteristics (Eley, 2019).

The rheology of paint is generally improved by the addition of thickeners or rheology modifiers (Xu et al., 2016), which can be grouped into three categories: Hydroxyethyl cellulose (HEC), non-associative and associative thickeners (Kästner, 2001). It has been proven that paints thickened by HEC and non-associative thickeners exhibit poor flow properties and storage instability (Kästner, 2001). Reuvers (1999) reported that if added in the correct amount, associative rheology modifiers are the most proficient type of thickeners because they interact with other paint components. Associative rheology modifiers are subdivided into Hydrophobically Modified Alkali Swellable Emulsions (HASE) and Hydrophobically Modified Ethoxylated Urethane (HEUR) (Bhavsar & Shreepathi, 2016; Jong, 2020).

It has been found that the thickening efficiency of HASE and HEUR thickeners is mainly influenced by their interaction with the binder used in the paint formulation (Xu et al., 2016; Quadrat et al., 2001). There is therefore a need to study the influence of the type and the amount of binder on the overall rheology of paint containing HEUR and HASE thickeners. There are four types of binder used in the production of water based paint namely; pure acrylic, styrene-acrylic, vinyl-acrylic and vinyl acetate butyl acrylate binders (Wojciechowski et al., 2015). Many research studies have been published on the weathering conditions (UV stability), durability and optical properties of the films of paint made of each binder type. For instance, Melchiorre Di Crescenzo et al., (2014) and Wojciechowski et al., (2015) found that paints containing pure acrylic and styrene acrylic binders experience less degradation under accelerated weathering conditions. Tiarks et al., (2003) reported, that irrespective of the type of binder used, the pigment / binder ratio also called pigment volume concentration (PVC) is an important parameter of paint because it determines the gloss, scrub resistance and tensile strength of the applied layer of paint.

Although considerable research has been done studying the influence of the type of binder on the durability of water-based paints, not much research has been done on the rheological responses of water-based paints thickened with associative rheology modifiers in the presence of each binder type. Similarly, the influence of the type of binder, rheology modifiers and their concentrations on the optical properties of water-based paints has not been thoroughly investigated in the literature.

This project will use rheology as a tool to study the efficiency of HASE and HEUR rheology modifiers at different concentrations in a formulation of water-based paint. This will be done in the presence of the two prevalent binders used in the formulation of decorative water-based paints namely; pure acrylic and styrene acrylic binders. Additionally, this project will investigate the effect of rheology modifiers, their concentration, and the type of binder on optical properties of paints such as opacity and gloss.

The outcomes of this research will facilitate an appropriate selection of the binder and thickener concentration, as well as optimising paint formulation by correlating rheological data to properties such as storage stability, levelling, and sag resistance.

1.2. The research problem

It has been proven that associative rheology modifiers can improve the flow and deformation of water based paints because they interact with other paint constituents; mainly the binders (Reuvers, 1999). However, Kostansek (2003) reported that the effectiveness of associative rheology modifiers is affected by slight changes of paint components. Therefore, there is a need to predict the effect of changes in the concentration and type of key constituents of paints on the flow and deformation properties. The influence of the binder type, thickener type and thickener concentration on the rheology and some optical properties of water-based paints is also not well understood.

1.3. Research questions

The expected outcome of this research project is the understanding of water-based paints properties using Rheology. This outcome will be achieved by establishing a relationship between rheological parameters and the properties of water-based paints. It is proposed that the success of paint systems depends greatly on satisfying specific flow and deformation requirements (Crawford & Meyer, 2019). Effective application and film formation necessitate a high degree of flow and hence the rheological properties must be linked to the application and the final film of the coating (Eley, 2019).

Proving the validity of this hypothesis will require answering the following research questions:

- i. What are the effects of the type and concentration of associative rheology modifiers (i.e., HASE and HEUR) on the overall rheology profile of the water-based paint?
- ii. How does the binder type affect the thickening efficiency of water-based paint, using HEUR and HASE rheology modifiers?
- iii. Is there a relationship between rheology and the gloss and opacity of water-based paints?

1.4. Aim and objectives

The aim of this research is to investigate the rheological parameters such as viscosity, viscoelasticity and thixotropy of water-based paints, using rheology modifiers in the presence of pure acrylic and styrene acrylic binders. The following objectives must be met:

- i. To study the effect of pure acrylic and styrene acrylic binders on the flow and deformation of water-based paints thickened by HEUR and HASE associative thickeners.
- ii. To determine the effect of the thickener's concentration on the rheological parameters and to optimise paint properties such as in-can stability, levelling and sag resistance.
- iii. To investigate the impact of some rheology modifiers on key optical properties of paint such as gloss, opacity and hiding power.

1.5. Approach

A total of twelve experimental samples were prepared, based on an existing formulation of a white decorative water-based paint. The experimental samples can be grouped into 2 categories, namely paint samples containing pure acrylic (PA) and those containing styrene acrylic (SA) binder. For each type of binder, the effect of thickener concentration was investigated by preparing samples of paint thickened with HASE and HEUR rheology modifiers at the concentration range of 0-1.2 %. The effect of rheology on the optical properties of paint was also investigated. The rheological characterisation of experimental samples was conducted using the Discovery HR-3 Hybrid rheometer from TA instruments. The rheological data obtained was then analysed and correlated to the paint properties.

1.6. Significance of the research

This Rheological study presents a significant economic advantage for the paint industry. Various experienced paint formulators confirmed that most of the total cost of new product development is consumed in attaining an adequate product rheology (Eley, 2005; Eley, 2019). Therefore, understanding the impacts of rheological parameters on the performance of water-based paints is an important tool in optimising and improving their formulation.

Although the performance of organic solvent based paints is superior to the water based ones, they negatively impact the environment by releasing strong odour and toxic compounds into the atmosphere (Reuvers, 1999). Firmer environmental regulations have reduced the manufacture of organic solvent paints. Therefore, the production of water-based paints presents important environmental and health benefits such as lower Volatile Organic Compounds (VOC), low odour and less hazardous disposal. Extensive research is required in order to make the flow and performance of aqueous paints comparable to that of the organic solvent paints.

1.7. Delineation

- This research involves only one formulation of a decorative white paint.
- The type and concentration of the rheology modifiers and binder type in the experimental paint sample were varied but the type and concentration of other raw materials were kept unchanged.

1.8. Terminology

Binder: a polymer latex used in water-based paints that holds pigment particles and additives and promotes a uniform layer when paint is applied and dried.

Ease of application: A characteristic of paint that allows for easy application using a roller or a brush. Ease of application is often referred to as brushability.

Durability: the ability of paints to withstand certain environmental or chemical conditions.

Gloss: the optical reflectance characteristics of a surface of a coating.

Levelling: the ability of paint to yield an even film when applied on a substrate

Opacity: the degree to which a paint obscures or hide a surface.

Pigment: any white or coloured fine, solid particle, insoluble in the liquid medium in which it is dispersed.

Sagging: the excessive flow of paint down a vertical surface under gravity causing irregularities.

1.9. Organisation of the dissertation

The thesis is sequenced as follows:

Chapter 1: Introduction

This chapter gives a background of water-based paints and contains the aim, the objectives and the significance of this research. Additionally, this chapter encompasses the research questions and provides a brief approach on how the aim and objectives of this work were met.

Chapter 2: The Literature review

Chapter 2 includes theory on the principles of rheology as well as fundamentals of water-based paints raw materials and formulation. It also contains the findings of previous research on the rheology of paints.

Chapter 3: Research methodology

This chapter describes the experimental materials, the water-based paint preparation procedure and the rheological test specifications. It further outlines the data production and the techniques used to analysis empirical data.

Chapter 4: Results and discussion

Chapter four deals with the discussion of results obtained from the rheological tests and paint optical tests. It seeks to relate rheological data to paint performance properties such as flow, levelling, sag resistance, ease of application and storage stability.

Chapter 5: Conclusion and recommendations

The final chapter of this study encompasses concluding remarks and recommendations based on the findings.

Bibliography

In this section all the literature consulted for this research is listed.

Appendices

The appendices include all the raw data generated, the procedures followed, and the equations used in analysing the empirical results.

CHAPTER TWO

THE LITERATURE REVIEW

2.1. Introduction

This chapter includes theory on the principles of rheology and the correlation of certain rheological parameters such as viscosity, viscoelasticity, and yield stress to the characteristics of paints. This section provides information on paint raw materials and their influence on rheology and on the properties of water-based paints. The rheology modifiers or thickeners are the additives that are generally used to improve the flow properties of paints described in this chapter. Furthermore, the composition, thickening mechanisms and factors affecting the performance of HASE and HEUR rheology modifiers in water-based paints formulation are discussed.

2.2. Rheology fundamentals

Rheology is the study of the flow and deformation of matter when exposed to external forces (Mezger, 2006). Ideal solids or elastic materials store the energy conveyed to them by an external force and use it to re-establish their original shape after the force is removed. Ideal fluids or viscous materials dissipate the energy imparted to them by the external force by flowing and by releasing thermal energy. Substances that exhibit both elastic and viscous behaviours are called viscoelastic materials (Schramm, 1994).

2.2.1. Flow behaviour

Figure 2.1 below is called the two plates model and is usually used to describe the basic concepts of rheology for viscous fluids. The bottom plate is static while the shear stress acts on the upper plate with shear area (A). The liquid sample is sheared in the space between the two plates and h is the distance between the plates.

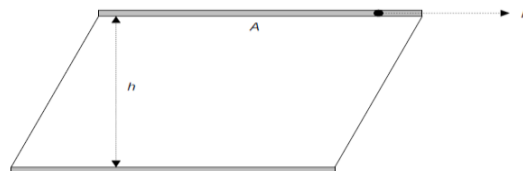


Figure 2.1: Two plates model (Mezger, 2006)

The shear force acting on a surface area A unit is termed **shear stress** (σ) and is given by the following expression (Alderman, 2016).

$$\sigma = \frac{F}{A} \quad (2.1)$$

The ratio of the upper plate velocity to the distance between the plates is termed **shear rate** ($\dot{\gamma}$) and is expressed as follows (Mezger, 2006) :

$$\dot{\gamma} = \frac{v}{h} \quad (2. 2)$$

For Newtonian fluids also called ideal viscous fluids, at constant temperature, the proportionality between the force applied (shear stress) and the fluid velocity (shear rate) is constant. This proportionality constant is referred to as the **viscosity** (η) of the fluid (Mezger, 2006). It is the measure of the resistance against any permanent deformation involved in flow (Eley, 2019).

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (2. 3)$$

2.2.2. Elastic behaviour

In the case of elastic solids at constant temperature, the ratio of the force applied or shear stress σ to the resulting displacement or deformation γ is a material constant called **shear modulus** (G). The shear modulus defines the elasticity behaviour of the material (Schramm, 1994; Eley, 2006).

$$G = \frac{\sigma}{\gamma} \quad (2. 4)$$

2.2.3. Viscoelasticity

Materials that exhibit both viscous and elastic behaviours when exposed to a deformation are termed viscoelastic materials (Gould et al., 2019). For viscoelastic materials such as water-based paints, the shear strain and shear stress are not in phase, resulting in a delay to deformation (Becker & Nagel, 2010). This delay between the strain and the stress is referred to as phase shift (Becker & Nagel, 2010). Rheological characterisation of viscoelastic materials is done by controlled shear deformation (CSD) tests or oscillatory tests, by determining the phase shift angle δ ($0^\circ < \delta < 90^\circ$). The phase shift angle will give an indication on the delay of the deformation. For instance, if δ is close to 0° , the material has minor delay to deformation; hence the material is predominantly elastic. For ideal elastic material $\delta=0^\circ$. If δ is approaching 90° , the material has greater delay to deformation i.e., the viscous behaviour is predominant. Newtonian fluids have $\delta=90^\circ$ (Spaull, 2007). The elastic and viscous behaviours of a viscoelastic material are described by the storage modulus (G') and the loss modulus (G''), respectively. The ratio of G'' to G' is called the loss factor ($\tan\delta=G''/G'$) and is used to quantify the amount of energy dissipated during the deformation (Becker & Nagel, 2010). Hagan et al. (2010) and Hagan et al. (2011) found that pigment such as TiO_2 and

extenders like kaolin and CaCO_3 which are used in the manufacture of paints have a large influence on the viscoelasticity of water-based paints. Similarly, Prall (2000) found that the viscoelasticity of water based paint is not only dependent on the pigment volume concentration (PVC), but also on the type of extender used in the formulation. The storage modulus of water-based paint was found to increase with increases in PVC and the paint formulated with clay as an extender was reported to have higher storage modulus than the formulation containing CaCO_3 (Prall, 2000).

2.2.4. Yield stress

The Yield stress of a material is defined as the minimum force required to be applied to this material in order to initiate flow (Barnes, 1999; Eley, 2005). The study of yield stress in structured fluids such as paints was proved to be crucial in predicting their performance during their storage, their application and after application (Eley, 2006). Kästner (2001) reported that the presence of yield stress is an advantage for the in-can stability of water based paints, as it can prevent the sedimentation of pigment particles, but it can present a disadvantage to the flow and levelling of paints, after their application. Eley (2005) employed data from the Linear Viscoelasticity Range (LVER) of the strain sweep and frequency sweep, to establish that there is a relationship between the yield stress and the storage modulus of paints (Chen, 2000). Franck (2004) found that good flow and levelling of paints can be achieved if the yield stress is less than 0.25 Pa after high shear load, i.e., the application process. Furthermore, a combination of low shear rate viscosity exceeding 50 Pa.s and a yield stress greater than 1 Pa was determined to prevent pigment settling during the storage of paints (Franck, 2004).

The presence of yield stress can affect cost and paint manufacturing processes such as cavitation, freezing of valves and pumping (Eley, 2005). Rheological tests for determination of yield stress include the steady state stress sweep test, the steady state rate sweep from high to low shear rates test and the Dynamic Strain Sweep test (Chen, 2000). The latter test is suitable for determining the yield stress of high viscosity and highly viscoelastic materials, while the former tests are suitable for yield stress analysis for medium and low viscosities materials, respectively (Chen, 2000). Additionally, the yield stress measurement can be performed by the curve fitting method and the extrapolation method by fitting certain rheological models (Eley, 2006). Eley (2005) found that oscillatory strain sweeps, also called amplitude sweep tests, are more effective rheological tests in determining the yield stress than the stress ramp test. Moreover, it was established that the measurement of the yield stress by means of steady shear or oscillation strain sweep is more precise than curve fitting method (Eley, 2019). The curve fitting method is imprecise because it uses the viscosity data to predict the solid-state property of a structured fluid (Eley, 2019).

2.3. Rheology and water-based paint performance

Due to the complexity of its composition, water-based paint is generally non-Newtonian i.e. the viscosity is not constant but depends on the shear rate (Glass & Prud'homme, 1997). However, Eley (2019) recently reported that the flow of paints is controlled by the shear stress, not the shear rate. Thus, accurate predictions of paint performance can be achieved from the viscosity-shear stress plots (Eley, 2019). The non-Newtonian character of water based paint can be adjusted by the addition of thickeners, in order to improve its properties (Glass & Prud'homme, 1997). All key properties required from paints such as levelling, sag resistance and storage stability are controlled by their rheological characteristics (Kästner, 2001, Moolman, 2003, Bhavsar & Shreepathi, 2016, Eley, 2019).

2.3.1. Levelling

Levelling is the ability of paint to yield an even film when applied on a substrate. This is an important aspect because it has an impact on the optical properties of the dry film, such as colour, opacity, gloss etc. (Overbeek et al., 2003). Levelling is a complex characteristic of paint because it depends on many factors such as evaporation, wicking, viscosity, surface tension and viscoelasticity (Eley, 2019). Kästner (2001) found that the levelling of water-based paint is greatly influenced by the type of rheology modifiers used and the PVC of the formulation. It was shown in previous studies that associative rheology modifiers produce better flow and levelling than ASE and HEC thickeners because of the difference in the thickening mechanisms (Kästner, 2001; Bhavsar & Shreepathi, 2016).

According to Kästner (2001), water based paint with PVC greater than 50% will level poorly after its application because of the strong solid-character. TA Instruments (2015) reported that paint levelling is greatly influenced by its viscosity and the yield stress, and it can be predicted by using the strain sweep test. Results from strain sweeps by TA Instruments (2015) illustrate that good levelling of water based paint can be achieved between the viscosity of 25 and 35 Pa.s at a 25% strain. Bhavsar and Shreepathi (2016) showed that the levelling of water-based paints takes place within the first three minutes after application. Thus, the viscosity recovery during the first three minutes after application will give an indication on the paint levelling. In another study, Bhavsar and Shreepathi (2016) suggested that paint with good levelling must have a viscosity greater than 25 Pa.s at a shear rate of 0.085 s^{-1} and a yield stress smaller than 0.25 Pa. Furthermore, levelling of water-based paint is influenced by the elastic shear modulus and relaxation time. A relaxation time of between 40 and 50 seconds, as well as a gradual increase of the elastic shear modulus with the increase in shear rate will lead to proper levelling (Bhavsar & Shreepathi, 2016). The rheological measurement of levelling of paint can

be achieved by using the three interval thixotropy test (3ITT) describing structure recovery of paint. This method is suitable because it can correlate the application and post application behaviours of paint (Paroline, 2016).

2.3.2. Sagging

Sagging is referred to the excessive flow of paint down a vertical surface under gravity, causing irregularities on the film (Lade et al., 2015). It is generally influenced by the gravitational stress (σ_g) which is given by the following equation (Lade et al., 2015; Eley, 2019).

$$\sigma_g = \rho g h \cos\theta \quad (2.5)$$

Where, $\cos\theta = 1$, for a vertical surface for. ρ is the density of the paint, g is the gravitational acceleration and h is the wet film thickness.

Any paint will resist sagging if the gravitational shear stress remains inferior to the yield stress σ_g (Eley, 2005; Eley, 2019). Therefore, sagging can be predicted by first calculating the gravitational stress from equation 2.5, then by finding the governing sagging viscosity from a plot of viscosity versus shear stress (Eley, 2019). Franck (2004) and Moolman (2003) found that sagging is influenced by the paint viscosity at low shear rates. However, other authors suggest that sagging and levelling are influenced by the type of surface, and therefore, rheological characterisations at low and high shear rates are required, in order to predict sagging of paint (Bhavsar & Shreepathi, 2016). Bosma et al. (2006) and Lade et al. (2015) reported that yield stress and thixotropic behaviours can be beneficial in preventing sagging and enhancing paint optical properties. By contrast, Eley (2005) found that the presence of yield stress can be disadvantageous in sag resistance mostly when there is an excessive decrease of the paint viscosity at the critical stress level. Recently, Jiang et al. (2018) used the creep test to predict sagging for water-based paints and it was established that lower creep compliance values which lead to more than 90 percent of the paint structure recovery, are favourable for sag resistance. Lower creep compliance implies stronger structure and hence greater recovery after application (Jiang et al., 2018). This desired low creep compliance can be achieved by the addition of rheology modifiers to water based paint formulations (Jiang et al., 2018).

2.3.3. Storage stability and shelf life

Generally, the storage stability of water based paint is associated with viscosity at a low shear rate (Crawford & Meyer, 2019). But this viscosity does not offer enough information to fully comprehend the complex phenomena of pigment particles sedimentation under gravity, and its impact on the long-term shelf life (Armelin et al., 2006). The stability of paint is greatly

influenced by the type or combination of surfactants used in the formulation and the size of pigment particles (Haramagatti et al., 2018).

Bhavsar et al., (2013) reported that the stabilisation of dispersed pigments particles in a paint formulation is a complex phenomenon and suggested that a proper selection or combination of dispersant and wetting agents is crucial for the long-term stability of paint.

Bhavsar et al. (2013) used creep recovery, amplitude sweep and accelerated stability tests to study the storage stability of paints. The authors found that the determination of yield stress is not useful in predicting the stability of paint and that the loss factor gives a better indication of pigment settling.

The creep recovery test is one of the rheological tests that can predict the stability of a paint system because the data from this test can correlate viscosity, deformation and settling of pigment particles (Haramagatti et al., 2018). Furthermore, oscillatory amplitude sweep, and oscillatory frequency tests can also be used to predict the stability of paints.

Haramagatti et al. (2018) found that higher storage modulus (G') is favourable for the stability because greater G' implies that the paint is predominantly elastic, which infers that the paint has high structural strength. It has been empirically determined that good storage stability of a structured fluid can be achieved if $\tan\delta$ ($\tan\delta = G''/G'$) is less than one (Laxton & Berg, 2008). Other Rheological parameters such as critical strain (γ_c) and LVER can be used to evaluate the internal energy of the structure of the system of a dispersion also called the “cohesive energy” (E_c) (Haramagatti et al., 2018).

According to Crawford and Meyer (2019) the presence of yield stress can prevent the particles from settling and improve shelf-life stability. Yield stress of paint can be evaluated by a stress-controlled rheometer, by applying slight stresses on the paint. If the paint undergoes no displacement i.e. very low shear rate, this implies that the stress applied is below the yield stress and if the fluid experiences greater shear rates, that means that the applied stress has exceeded the yield stress of the system (Wadud, 2003).

2.3.4. Ease of application

Paint application generally occurs at high shear rates above 1000 s^{-1} (Chatterjee et al., 2019). Ease of application or brush ability is greatly favoured by low viscosity at high shear rates (Overbeek et al., 2003; Crawford & Meyer, 2019).

However, Chatterjee et al.(2019) found that the viscosity at high rate is not sufficient for predicting the ease of paint application and suggested that the sign of the first normal stress

(N1) of paint provides more comprehensive indication on the properties of paint at high shear rates.

It was determined that a negative normal stress indicates that compressive force drawing the brush towards the surface resulting in an ease of application of paint i.e., low brush drag. A positive normal stress on the other hand indicates a tensile force pulling the brush away from the surface and hence additional force is required to counter this tensile force (Chatterjee et al., 2019).

2.4. Water based paint formulation

The main components of water based paints are water, pigments, polymeric binder and property enhancing additives (Tiarks et al., 2003; Alua, 2012; Höfer, 2012). The pigment is the water insoluble solid particles that are responsible of imparting colour, opacity and mechanical strength to the paint layer (Karakaş et al., 2015; Bottomley & Spoor, 2017; Costa et al., 2017; Sun et al., 2018). Many researchers found that the protective and decorative properties of paint are impacted by the pigment volume concentration (PVC) (Tiarks et al., 2003).

The PVC is an important parameter of paint because it controls the gloss, scrub resistance and tensile strength of the applied layer of paint. Kästner (2001) determined that high PVC can render the rheology of water-based paints complex by inducing less viscous behaviour and it can negatively affect flow, levelling, and sag resistance.

Binders are polymer latexes used in water based paints (Mariz et al., 2010). They are responsible for the formation of the film that holds together the homogeneous mixture of pigment particles and additives and promote a uniform layer when the paint is applied (Mariz et al., 2010; Gaggero et al., 2021). Furthermore, the binder affects properties such as the toughness and gloss of the dried film (Alvarez & Paulis, 2017).

Pure acrylic (PA) and styrene acrylic (SA) are the commonly used binders in the manufacturing of decorative water based paints. Melchiorre Di Crescenzo et al. (2014) and Wojciechowski et al. (2019) found that water-based paints formulated with pure acrylic and styrene acrylic binders experience less degradation under weathering conditions.

Additives are incorporated in water based paint in small amounts, in order to improve properties of paint during manufacturing, while in storage, during application and after application (Svanholm et al., 1997; Moolman, 2008). The roles of different additives used in water-based formulation are given in Table 2.1 below.

Table 2.1: Water-based paint additives

Additives	Role
<i>Thickeners or rheology modifiers</i>	Are added to improve in-can stability, application and post application properties (Svanholm A' et al., 1997; Kästner, 2001; Moolman, 2003; Jiang et al., 2018).
<i>Coalescent or plasticers</i>	Are used in paints to allow film formation of the polymeric binder particles. This is achieved by unstiffening the latex particles and allowing them to yield a smooth and uniform surface finish (Chen et al., 2017; Durand et al., 2010).
<i>Surfactants or wetting agents</i>	Enhance paint properties such as shelf life and mechanical stability by reducing the free energy of different interfaces (Hellgren et al., 1999).
<i>Dispersants or dispersing agents</i>	Are added to inhibit agglomeration and flocculation of pigment particles dispersed water. The stabilisation of pigment particles is achieved by the adsorption of dispersants on the particles surface by steric and/or electrostatic methods (Farrokhpay et al., 2010).
<i>Fungicides</i>	Are used to prevent bacteria growth (Moolman, 2008).
<i>Defoamers or antifoaming agents</i>	Are used in paint formulations to remove foam by breaking the air bubbles formed during mixing (Knoef, 1992).

2.5. Rheology and water-based paint raw materials

In this section, most of the water-based paint raw materials and their influence on the flow and deformation of paints are discussed.

2.5.1. Pigments and extenders

In the paint industry, a pigment is defined as any white or coloured fine, solid particle, insoluble in the liquid medium in which it is dispersed, during the manufacturing of paints (Lambourne & Strivens, 1999). Pigments provide optical properties such as colour and opacity by scattering or absorbing light (Sun et al., 2018). Titanium dioxide (TiO₂), due to its high refractive index and hiding power, is the most prevalent white pigment used in the manufacture of paints (Karakas et al., 2015; Costa et al., 2017; Löf et al., 2020). An extender or pigment filler is a pigment with poor optical properties and is usually at a lower cost (Lambourne & Strivens, 1999). Extenders are added to paint formulation to decrease the high cost of TiO₂ (Karakas et al., 2015).

Pigments and extenders transform the rheology of water based paints, by creating strong shear thinning, during yield stress, viscoelasticity and thixotropy (Kästner, 2001; Moolman, 2008). They reduce the viscous behaviour i.e. they induce a more elastic character by increasing the volume fraction of solids in a paint system (Kästner, 2001). The advantage of the solid-like character imparted to water-based paint by pigments and extenders is the improvement of the high shear viscosity and provision of an adequate support for the film

build. However, this character can reduce the open time and hence negatively affect the levelling of paint (Kästner, 2001).

2.5.2. Surfactants or wetting agents

Surfactants are paint additives that enhance paint properties such as shelf life and mechanical stability (Butler et al., 2005) by wetting the pigment particles and preventing their agglomeration (Hellgren et al., 1999). Haramagatti et al. (2018) reported that surfactants affect the rheology and other film properties of water-based paints such as water sensitivity and scrub resistance. Surfactants have a substantial effect on the rheology profile of paints because their adsorption onto the binder particles is similar to the adsorption of associative rheology modifiers (Hellgren et al., 1999; Mahli et al., 2005). Surfactants and rheology modifiers act simultaneously onto the binder particle surface, which results in a poor association of the rheology modifiers (Glass, 1999; Hellgren et al., 1999; Mahli et al., 2003). Consequently, greater amount of surfactants in a water based paint formulation will displace the molecules of associative thickener adsorbed in the binder particles; resulting in a significant decrease of the paint viscosity in the low shear rate region, but the viscosity in the high shear rate region remains unchanged (Glass, 1999; Osterhold, 2000). The extent of the decrease of the viscosity in the low shear rates region depends on the quantity and category of surfactants used in the coating formulation (Osterhold, 2000).

There are two types of surfactants used in the manufacture of water based paints, namely ionic and non-ionic surfactants (Haramagatti et al., 2018). Ionic surfactants adsorb on the pigment particle, are relatively low in molecular weight and contain charged hydrophilic groups. Ionic surfactants stabilize pigment particles by means of electrostatic repulsion (Hellgren et al., 1999; Butler et al., 2005; Mewis & Wagner, 2011; Haramagatti et al., 2018), while the non-ionic type achieve stabilization of particles by steric repulsion (Butler et al., 2005; Haramagatti et al., 2018).

2.5.3. Dispersants

Dispersants or dispersing agents are substances that are added to water paints to inhibit agglomeration and flocculation of pigments particles dispersed in water (Weyershausen & Lehmann, 2005; Löf et al., 2020). The stabilisation of pigment particles is achieved by the adsorption of dispersants on the pigment particles' surface by steric or/and electrostatic methods (Clayton, 1998; Hellgren et al., 1999). Löf et al.(2020) found that dispersants can influence the drying of paint and reduce the consumption of TiO₂ in the production of water-based paints. There are three types of dispersants, namely ionic, anionic, and cationic. The adsorption of ionic dispersants provides an electrical charge to the pigment particle surface

(Hellgren et al., 1999). In steric stabilisation the pigment particles that are adsorbed polymeric species are compatible with the solvent that extends outward from the particle surface, creating a physical barrier (Hellgren et al., 1999). Anionic dispersants are mostly potassium polyphosphate derivative and are generally used to stabilise titanium dioxide pigment particles. This class of dispersants conveys negative charge to the pigment particles by the adsorption of phosphate anions, causing mutual electrostatic repulsion of the binder and pigment particles. Cationic dispersants are not widely used in the aqueous medium. They stabilise pigment particles based on the quaternary nitrogen compounds (Hellgren et al., 1999).

Most dispersing agents will facilitate the interaction of pigment particles with rheology modifiers and the binder (Kästner, 2001). The interaction and non-interaction between associative thickeners and pigment particles is mostly dictated by a proper selection and/or combination of dispersants. An absence of proper interaction between the thickener and pigment particles results in phase separation and flocculation taking place; thus yielding low gloss and poor flow (Hellgren et al., 1999; Kästner, 2001).

2.5.4. Binders

Binders are aqueous dispersions of emulsion polymer particles referred to as latexes used in water based paints (Eley, 2005; Mariz et al., 2010). They are responsible for the formation of the film, hold together the homogeneous mixture of pigment particles and additives and promote a uniform layer when paint is applied (Mariz et al., 2010; Alua, 2012; Gaggero et al., 2021). The amount and type of binder in a paint formulation affects properties such as toughness, adhesion and gloss of the dried film after paint application (Alvarez & Paulis, 2017). Furthermore, the thickening efficiency of associative rheology modifiers can be impacted by the type of binder present in the paint formulation (El-Wahab et al., 2019). Pure acrylic and acrylic styrene polymers are the commonly used binders in the manufacturing of water based paints (ŠňUpárek et al., 2005). They are synthesized by emulsion polymerization process of acrylate ester monomers and the esters of acrylic acid (ŠňUpárek et al., 2005). Pure acrylic binders are made of methyl methacrylate ester monomers and esters of acrylic acid, while styrene binders are based on styrene monomers polymerized with acrylic acid esters (ŠňUpárek et al., 2005). Binders require the addition of coalescent which produces an acceptable minimum film formation temperature (MFFT), good elasticity and UV resistance (Alvarez & Paulis, 2017). Styrene acrylic binders, unlike pure acrylic ones, are less resistant to UV radiation. They undergo photo oxidation by solar radiation, causing the paint film to turn yellow over time (El-Wahab et al., 2019). The interactions between the binder particles (latex) and associative thickeners form a network which generally results in an increase of viscosity

of water based paints (ŠňUpárek et al., 2005; Bhavsar & Shreepathi, 2016; Ibrahim et al., 2019). Polverejan (2017) and El-Wahab et al. (2019) established a relationship between the latex particle size and the thickening efficiency of water based paint, using associative thickeners. It was found that the smaller the latex particle size, the higher the hydrophilicity (Polverejan, 2017) and the greater the thickening efficiency of associative thickeners is, because there is a large surface area for interaction (El-Wahab et al., 2019). It has been reported that paint formulated with a binder with small particle size exhibited better optical, protective and application properties (Xu et al., 2016; Alvarez & Paulis, 2017; El-Wahab et al., 2019). ŠňUpárek et al. (2005) found that a pure acrylic binder produces higher viscosity and pseudoplasticity than a styrene acrylic binder at the same associative rheology modifier concentration. Styrene based binders are more hydrophobic than methyl methacrylate based ones (pure acrylic) binder (Fardi et al., 2018), this hydrophobicity hinders water penetrability to latex particles, resulting in lesser swelling of particles and limited carboxylic group detachment (Quadrat et al., 2005; Xu et al., 2016).

2.5.5. Coalescents

Coalescents also referred to as plasticizers are used in aqueous paints to allow film formation of the polymeric binder particles (Durand et al., 2010; Höfer, 2012). This is achieved by softening the latex particles and allowing them to yield a smooth and uniform surface finish (Chen et al., 2017). Coalescing agents have a great impact on rheological characteristics; mostly on drying, levelling and sag resistance (Svanholm et al., 1997). Generally, the addition of coalescent to aqueous paints induces a rise in viscosity. It is hence proposed by some reviews that coalescing agents can be used as rheology modifiers in addition to acting as thickeners; because of their considerable impact on levelling and sagging during film formation (Svanholm et al., 1997).

2.5.6. Defoamers

Defoamers or antifoaming agents are substances with low surface tension and are generally insoluble in the water used in paint formulations, to remove foam (Höfer, 2012). The addition of defoamer into a paint system induces a slight rise in viscosity due to the solubilisation in the micelle, yielding a larger volume and more interactions between micelles (Knoef, 1992).

2.5.7. Rheology modifiers

Rheology modifiers or thickeners are added to water based paints to improve in-can stability and application properties (Bhavsar & Shreepathi, 2016). There are three categories of

thickeners used in aqueous coatings, namely; hydroxyethyl cellulose (HEC), non-associative and associative thickeners (Rhulmann et al., 2016).

HEC or cellulosic thickeners are the traditional type of paint thickening agent. They are non-ionic water soluble and produce pseudoplastic (shear-thinning) behaviour in aqueous paints (Kästner, 2001). They present various disadvantages including poor spatter resistance and they are subject to bacterial and enzyme attack, with consequent viscosity loss, affecting other flow properties such as levelling and sagging (Maestro et al., 2002).

In order to counter the inadequacy of HEC thickeners, non-associative thickeners also known as alkali soluble emulsions (ASE) were developed. They are synthetic polymers inducing pseudoplastic and elastic behaviour to water based paints (Bhavsar & Shreepathi, 2016). However, ASE presents disadvantages related to paint instability; and a high concentration of ASE is required in order to achieve acceptable flow properties (Polverejan, 2017).

Associative rheology modifiers thicken water based paints through self-association and hydrophobic interaction with other paint components such as surfactants, binder and pigment particles (Emélie et al., 1997; Karlson et al., 2000; de Souza et al., 2017). All associative rheology modifiers possess hydrophobic moieties at the end of their hydrophilic macromolecular chains, which enables them to interact with their own molecule and other paint ingredients (de Souza et al., 2017). They are subdivided into hydrophobically modified alkali swellable emulsions (HASE) and hydrophobically modified ethoxylated urethane (HEUR) (Bhavsar & Shreepathi, 2016). The thickening mechanisms and synthesis of HASE and HEUR are not entirely the same. HASE thickeners are very acidic anionic associative polymers manufactured by emulsion polymerization of methacrylic acid (MAA), ethyl acrylate (EA), and a small amount of hydrophobic macromonomer, as shown in Figure 2.2 below (Hernández-Baltazar et al., 2004; Dundua et al., 2014).

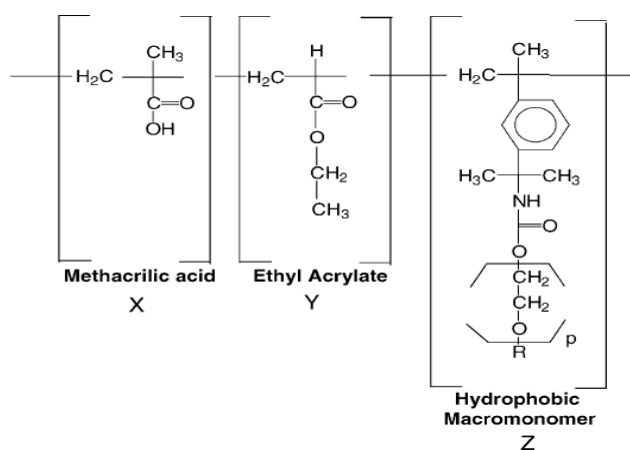


Figure 2.2: Molecular structure of model HASE associative polymer (Hernández-Baltazar et al., 2004)

The macromonomer is an amphiphilic compound (partially water soluble) in which the strongly hydrophobic segments (generally a long alkyl chain) are separated from the polymerizable double bond by water soluble polyethylene glycol (PEG) (Dundua et al., 2014). The thickening with HASE is mainly due to swelling and an increase of the hydrodynamic volume of the HASE particles at a pH above 7, which decreases the volume available for binder particles and neutralizes the carboxyl groups of the latex particles, resulting in an increase of viscosity (Quadrat et al., 2003, Hernández-Baltazar et al., 2004, dos Santos et al., 2007, Dundua et al., 2014, de Souza et al., 2017). Thickening water based paints with HASE usually result in a presence of yield stress, and pseudoplastic and thixotropic behaviours originating from ionic bonds between the carboxylic functions of the polymer and water molecules (Bhavsar & Shreepathi, 2016). Furthermore, the performance of HASE thickeners results from the steric and electrostatic repulsion forces between dissociated carboxylic groups of binder particles and HASE rheology modifier particles (Quadrat et al., 2003). The thickening efficiency of HASE is mostly affected by the molecular weight of the hydrophobic end-groups (Karlson et al., 2000, Rhulmann et al., 2016), the amount of carboxyl present and the alkalinity of the medium (Quadrat et al., 2003; dos Santos et al., 2007). Hernández-Baltazar et al. (2004) reported that other substances such salts, surfactants and co-solvent can impact the performance of HASE in water-based paint formulations.

A molecule of HEUR rheology modifiers consists of a water soluble polymer backbone made of polyethylene glycol (PEG) units linked together with urethane groups and hydrophobic hydrocarbon moieties located at the ends of the PEG chain (Barmar et al., 2010; Yang et al., 2018). Figure 2.3 illustrates a typical structure of a HEUR rheology modifier, where R1 represent the hydrophobic end groups and the R urethane links.

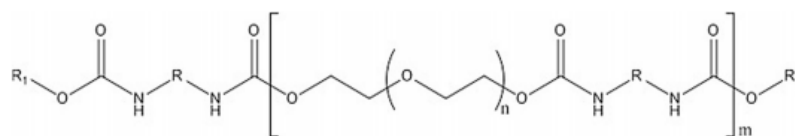


Figure 2.3: Molecular structure of HEUR rheology modifier (Yang et al., 2018).

2.6. Thickening mechanisms of HEUR and HASE thickeners

The mode of action of associative rheology modifiers is principally based on their association through hydrophobic interaction with the binder particles (Bhavsar & Nehete, 2019). Some authors argue that associative rheology modifiers interact with their own molecule, as well as other paint ingredients such as surfactants and pigment particles (Emélie et al., 1997; Karlson et al., 2000; de Souza et al., 2017). All associative rheology modifiers possess hydrophobic moieties at the end of their hydrophilic macromolecular chains, which enable them to interact

with their own molecule and other paint ingredients (de Souza et al., 2017). They are subdivided into Hydrophobically Modified Alkali Swellable Emulsions (HASE) and hydrophobically modified ethoxylated urethane (HEUR) emulsions (Bhavsar & Shreepathi, 2016). The thickening mechanisms and synthesis of HASE and HEUR are not entirely the same (dos Santos et al., 2007).

The thickening with HASE in aqueous mediums is mainly due to the rise hydrodynamic volume and swelling of the rheology modifier particles (dos Santos et al., 2007) and by the association of hydrophobic groups with binder particles, forming a micelle-like aggregate that comes from ionic bonds between the carboxylic functions of the polymer and water molecules (Bhavsar & Shreepathi, 2016). According to Rhulmaan et al., (2016), the thickening efficiency of HASE is greatly affected by the molecular weight of the hydrophobic end-groups and the acid content.

HEUR rheology modifiers which are non-anionic, thicken by association of the hydrophilic groups in water and the adsorption of the hydrophobic groups on the surface of the binder particles, thus creating a link between latex particles, resulting in an increase in viscosity (Emélie et al., 1997; Quadrat et al., 2001; Yang et al., 2018). HEUR rheology modifiers provide good control of the flow and application properties of paint because the thickened system can progressively be destroyed when shear is applied (Quadrat et al., 2001). There are many factors affecting the performance of the HEUR thickeners; such as the size of the hydrophobic groups and the amount of surfactant present in the formulation (Emélie et al., 1997; Xu et al., 2016). Generally, if added at the correct concentration, HEUR thickeners improve the rheological features of the aqueous paint and hence induce excellent flow/levelling, gloss and sag resistance (Emélie et al., 1997; Reuvers, 1999; Xu et al., 2016).

Murakami et al., (1995) studied the impact of numerous HASE thickeners on the rheology profile of water-based paints formulated with a pure acrylic binder. It was established that, compared to HEC, all HASE rheology modifiers improved the viscosity in high shear rates. Kästner (2001) studied the thickening mechanisms of HEC, the non-associative and associative rheology modifiers, in the presence of an acrylic binder. The results showed that HASE and HEUR are more effective thickeners in terms of flow and levelling (Kästner, 2001).

2.7. Rheological models for paints

This section discussed four rheological models that have been used extensively in the flow analysis of different types of non-Newtonian substances. These models include Bingham, Casson, Power law and Herschel-Bulkley models. Although these models were effectively utilised to study the flow of paints, they present limitations in studying some rheological aspects of paints such as low shear region, thixotropy and elasticity, which are very significant

in studying the performance and application properties of paints (Eley, 2005). Furthermore, Eley (2019) indicated the limitations of these model equations for predicting the performance of paints because they only fitted a portion of most flow curves. Eley (2019) demonstrated that the important flow properties of paint are best understood as a function of specific shear stress ranges, not shear rate.

2.7.1. Bingham model

The Bingham model fits paints with a yield stress and is given by the following expression (Goodwin & Hughes, 2000; Osswald & Rudolph, 2015).

$$\sigma - \sigma_0 = \eta_p \dot{\gamma} \quad (2.6)$$

Where σ is the applied stress, σ_0 is the yield stress, $\dot{\gamma}$ is the shear rate and η_p is the plastic viscosity or the Bingham flow coefficient. According to Eley (2006) flow behaviour can be described by the Bingham model only when the applied stress is higher than the yield stress ($\sigma > \sigma_0$). A fluid with Bingham plastic behaviour possesses a non-zero yield stress level, above which there is a linear relationship between shear rate and shear stress (Alderman, 2016).

2.7.2. Casson model

The flow of dispersion model was derived by Casson which was said to fit numerous types of paint systems (Eley, 2006).

$$\sigma^{\frac{1}{2}} - \sigma_0^{\frac{1}{2}} = \eta_c^{\frac{1}{2}} \dot{\gamma}^{\frac{1}{2}} \quad (2.7)$$

The term η_c called casson viscosity. η_c is not an infinite shear viscosity but rather a limiting value and is approached at fairly high shear rates (Goodwin & Hughes, 2000; Osswald & Rudolph, 2015).

2.7.3. Power law

The power law or Ostwald-deWaele model was developed from the Newtonian law, by letting the exponent of the shear rate to be different to one and was given by the following equation (Eley, 2006; Alderman, 2016).

$$\sigma = K \dot{\gamma}^n \quad (2.8)$$

Where n is called "flow index". For shear thinning response the value of n is less than one and shear thickening behaviour is obtained for a value of n that is greater than one (Eley, 2006; Da Silva Siqueira et al., 2016). The Term K is dimensionless and is called the consistency

index; it has the numerical value of viscosity at shear rate equal to 1s^{-1} (Eley, 2006). The consistency index K describes the extent of a material's resistance to flow (Da Silva Sirqueira et al., 2016). Da Silva Sirqueira et al. (2016) utilised this model to study the shear thinning behaviour of water-based paint and found that Power law fits well to the rheological data of water-based paints. However, (Eley, 2005) reported that this model does not always give a good fit for the shear thinning behaviour of paints.

The disadvantage of power law is that it is not able to describe the flow properties for very low and very high shear rates. This model is, therefore, appropriate to describe the shear thinning behaviour at medium shear rates (Eley, 2005; Eley, 2006).

2.7.4. Herschel-Bulkley model

The power law behaviour above the yield stress is described by the Herschel-Bulkley model (Goodwin & Hughes, 2000; Osswald & Rudolph, 2015).

$$\sigma - \sigma_0 = K\dot{\gamma}^n \quad (2.9)$$

It was reported that the Herschel-Bulkley model describes the flow properties of paint types (Eley, 2005).

2.8. Rheological characterization for paints properties

This section deals with rheological tests and correlation of rheological parameters to paint properties, such as shelf-life stability, sagging and levelling. Rheological evaluation has two types of tests; namely rotational tests also called controlled shear rate (CSR) tests and oscillatory tests, or controlled shear deformation (CSD) tests (Eley, 2006; Mezger, 2006).

The viscosity curve which provides a relationship between viscosity and shear rate, or shear stress is a rotational test. Oscillatory tests discussed in this section include amplitude sweep and frequency sweep.

The former provides the relationship between viscoelastic functions (G' and G'') with increasing angular frequency, and the later test gives the relationship of G' and G'' with increasing strain. Finally, the three interval thixotropy test also known as 3ITT is discussed.

The 3ITT can be performed in the rotational mode or in both rotational and oscillatory modes. In the case where 3ITT is performed in rotational mode, the effect of time on viscosity is measured in all three intervals. When it is done in both modes, the change of G' and G'' with time, is measured in the first and the third intervals and the change of viscosity at constant shear rate is measured in the second interval.

2.8.1. Viscosity curve

The viscosity or flow curve described the behaviour of non-Newtonian fluids over a range of shear rate (Eley, 2006). Water based paint is shear thinning and the evaluation of the paint viscosity at different shear rates is significant in predicting critical paint properties (Crawford & Meyer, 2019). For instance, the low shear viscosity results can give an indication on the levelling, sagging and storage stability of paints. The viscosity data in the medium shear rate region can be used to investigate the pumpability, mixing and consistency of paints; while the high shear rate viscosity results can assess application properties of paints such as brushing and rolling (Franck, 2004). Cohu and Magnin (1996) found that low viscosity in the medium shear rate region is beneficial for ease of pumping of paints and a viscosity of 10 Pa.s at shear rate of 0.3 s^{-1} results in sagging of paint after application. Overbeek et al. (2003) established that an ease of application of paint using a brush or a roller can be achieved if the viscosity in the high shear region is in the range of 0.1 to 0.25 Pa.s. Low viscosities in the high shear rate region is not only beneficial for the ease of application (Kästner, 2001) but also for the gloss of the dry film of paint (Osterhold, 2000). Kästner (2001) argued that a film surface without brush marks can be attained if the low shear viscosity displays a Newtonian compartment.

It has been established in the literature that the viscosity of water based paints is greatly affected by the type and concentration of rheology modifiers used in their formulation (Kästner, 2001; Moolman, 2003). For instance, a HEUR rheology modifier was found to increase the viscosity of water based paint throughout the entire shear range, but the viscosity in the high shear rate regions was not affected by a change in HEUR concentration (Moolman, 2003), while a HASE rheology modifier was observed to produce higher high shear rate viscosity (Kästner, 2001). This indicates that a HASE rheology modifier leads to improved storage stability (Kästner, 2001); while the HEUR rheology will lead to storage instability but gives adequate levelling and flow properties (Moolman, 2003). Eley (2019) reported that important properties of paint such as application, storage stability, sag, levelling are governed by specific shear stresses, not shear rate. Shear stress, not shear rate is the correct independent variable for the graphical and experimental measurement of viscosity (Eley, 2019).

2.8.2. Amplitude sweep

The amplitude sweep is a controlled shear deformation test (CSD). CSD tests are performed under oscillatory mode by keeping the frequency constant (Eley, 2019). The amplitude sweep test is an important test for structured fluids such as water based paints, as it determines the linear viscoelasticity region (LVER) and quantifies the viscoelastic parameters (G' and G'') of a fluid over a range of shear deformation (Eley, 2006). Furthermore, this rheological test can

be used to measure the yield stress and the structure strength of paints (Eley, 2019). Sagging of paints can be predicted by comparing G' and G'' in the LVER. Paint can resist sagging if the G' is greater than G'' in the LVER i.e. the elastic behaviour is predominant in the LVER and paint is likely to sag if the viscous behaviour is dominant in the LVER (Cohu & Magnin, 1996). The data from an amplitude sweep can also give an indication on the shelf life of paint, by evaluating the G' at low strains. Good storage stability occurs if $G' > G''$ at low strains (Rudolph et al., 1996).

2.8.3. Frequency sweep

The Frequency Sweep Test is an oscillatory measurement which evaluates the behaviour of G' , G'' and the complex viscosity (η^*), as the oscillation frequency is gradually increased and the strain (found in the LVER) is kept unchanged (Eley, 2006). Quadrat et al. (2005) used the data from a frequency sweep to study the structure strength of water based paint. It was found that paint with lower storage modulus G' than loss modulus has weaker structure (Quadrat et al., 2005). The rate of the decrease of the complex viscosity with increase angular frequency gives an indication on the degree of shear-thinning of paint (Quadrat et al., 2005). Other paint properties such as spattering, storage stability, levelling and ease of application can be assessed by the frequency sweep test (Moolman, 2008). Flow and levelling can be assessed by determining the complex viscosity (η^*) in the low frequency zone. In general, paint systems with low complex viscosity present better flow and levelling properties (Hester & Squire, 1997). The spattering behaviour of paint can be evaluated at high frequencies because the paint application occurs at fast rates. Hence, if $\tan \delta (G''/G')$ is small at high frequencies, the paint shows a more plastic behaviour and hence will tend to spatter (Osterhold, 2000). Results from the frequency sweep below the critical strain can be useful to study the structural change of paint while in storage (Zhang et al., 2015). Higher values of $\tan \delta$ in the low frequency region imply that the paint's structure is weakly associated i.e., viscous flow is dominant, hence the inter-particle forces are weak to resist settling under gravity (Reuvers, 1999). Cohu & Magnin (1996) reported that paint can be applied effortlessly if the viscous behaviour is dominant i.e., $G'' > G'$ at high frequencies.

2.8.4. Three Interval Thixotropy Test (3ITT)

This test controls shear deformation and provides details on paint behaviour when exposed to great deformation, followed by small deformation (Osterhold, 2000). Bhavsar and Shreepathi (2016) proved that data from 3ITT can be used to predict the film build, levelling and sagging of paints. It was found that high viscosity in the second interval promoted higher paint deposition i.e., film build during application (Bhavsar & Shreepathi, 2016). Sagging and

levelling of water-based paints can be evaluated during the first 100 seconds in the third interval. Crawford and Meyer (2019) also found that 90 seconds after high shear was an acceptable time for paint to recover its initial viscosity. Bhavsar and Shreepathi (2016) disputed the idea that 100 percent viscosity recovery after high shear in a short period of time is an indication that paint will resist sagging and suggested that determination of the rate change in viscosity and speed of recovery between 10 and 100 seconds in the third interval, would predict sag and levelling of water based paints adequately. Better flow and levelling can be achieved when the change in viscosity between 10 and 100 seconds in the third interval is low (Bhavsar & Shreepathi, 2016). Sagging occurs when the coating needs a long time for the structural recovery after application (Osterhold, 2000). The sag resistant paint, therefore, has a quicker structure recovery time and a higher regenerated viscosity (Eley, 2006; Osterhold, 2000).

2.9. Paint optical properties

Optical properties are properties that affect the visual appearance of paint, which include colour, opacity, and gloss. This project seeks to determine the effect of HASE and HEUR thickener at different concentrations, and in the presence of styrene and pure acrylic binder, on the gloss and opacity of white decorative paint.

2.9.1. Gloss

Gloss is defined as the extent to which a dry film of paint reflects directed light (Farmand, 2012). The film of paint with high gloss reflects most of the light directed to the substrate; this is referred to as specular reflection, while substrate with low gloss or flatness reflects light in a non-specular direction (diffuse reflection) (Đurikovič & Ágošton, 2007). The gloss of a film of paint is greatly affected by the roughness of the surface, as defect on the substrate can alter the specular reflection of the light (Farrokhpay et al., 2010; Farmand, 2012). From a formulation point of view, Farmand, (2012) reported that the gloss of water based paint can be affected by interaction between thickener and other paint components such as binder particles and surfactant, the pigment particle size, the pigment distribution and the PVC of the paint formulation. It was found that gloss of water based paint decreases with increasing PVC (Farmand, 2012) because at lower PVC values there is a significant amount of binder present in the formulation and less pigment (Farmand, 2012). Farmand (2012) studied the effect of HEC and HEUR thickeners on the gloss of water-based paint. It was found that formulations of paint containing HEUR thickener resulted in higher gloss. Furthermore, the extent at which the pigment particles are dispersed can affect the gloss of paint. Therefore, the choice of the dispersant used in water based paint is crucial when high gloss is desired (Farrokhpay et al., 2010).

2.9.2. Opacity

Opacity or the hiding power of paint is the capacity of paint to obscure the colour of a substrate (Alua, 2012). The opacity of paint is achieved by blocking the light from the bottom of the paint film, which results in light scattering (Alua, 2012). Correspondingly, it has been reported that the opacity of paint is dependent on its intrinsic and perceived factors (Eley, 2005). The intrinsic factor is influenced by the adequacy of the dispersion and the stability of the pigment with light scattering characteristics (Höfer, 2012; Löff et al., 2020); while the perceived aspect of opacity is dependent on the quality of the layer of paint after application (Eley, 2005). For instance, a layer of paint with imperfect levelling generally results in irregularities in the film thickness and subsequently in poor hiding power (Eley, 2005). TiO_2 in the crystalline form is commonly used in paint manufacturing to enhance opacity, due to its high refractive index, which varies between 2.5 and 2.7 (Costa et al., 2017). Furthermore, TiO_2 promotes light scattering because of its narrow particle size (Costa et al., 2017). The Binders used in the formulation of water based paint do not affect the opacity of paint because they don't absorb or scatter light (Alua, 2012). Costa et al. (2017) and Karakaş and Çelik (2018) reported that the amount and type of dispersant used in water based formulations can affect the dispersion of TiO_2 and hence have an impact on the opacity. It was found that the use of amphiphilic block copolymers as dispersing agents can improve the dispersion efficiency of pigment particles, and hence improve opacity and other paint properties such as gloss and storage stability (Costa et al., 2017). Besides the pigment particle size and pigment dispersion, another factor influencing the opacity of white water based paint is the concentration of TiO_2 in the formulation (Alua, 2012).

CHAPTER THREE

RESEARCH METHODOLOGY

3.1. Introduction

This chapter discusses the different experimental materials, equipment, sample preparation procedure and rheological test conditions. Furthermore, it outlines the production of data and the techniques used to analyse empirical data.

3.2. Materials and equipment

3.2.1. Materials

The experimental samples of white decorative water-based paints were made-up of three groups of raw materials in an aqueous medium, namely pigments, polymeric binders, and additives. Pigments included titanium dioxide (TiO₂) as white pigment and filler pigments or extenders. The Polymeric binders employed included pure acrylic and styrene acrylic binders. Paint additives comprised dispersant, surfactant, pH adjuster, coalescing agent, defoamer, biocide and rheology modifiers.

3.2.2. Water paint recipe

The preparation of experimental paint samples was made according to the following recipe presented in Table 3.2 below.

Table 3.2: Water based paint recipe

Raw materials	Wt. %
Mill base stage	
Cold water	23.12
Dispersant	0.17
Surfactant	0.28
Anti-settling agent	0.35
White pigments (TiO ₂)	17.38
Extenders	12.80
Let down stage	
Binder (Styrene or Pure acrylic)	36.53
Coalescent agent	3.18
Opacifier	4.32
Biocide	0.38
Defoamer	0.21
5% Hydroxide solution (pH adjuster)	0.46
Rheology modifier (HASE or HEUR)	0-1.2

3.2.3. Equipment

Experimental samples were prepared using an electric laboratory cowles mixer in the quality control laboratory of Kansai Plascon in Epping Cape Town. The lab mixer is shown in Figure 3.4 below



Figure 3.4: Cowles mixer

The prepared paint samples were subjected to rheological evaluation using a Discovery Hybrid Rheometer (shown in Figure 3.5 below) in lab 1.17 in the department of Chemical Engineering at the Cape Peninsula University of Technology.



Figure 3.5: TA Discovery Hybrid Rheometer

The optical properties (gloss and opacity) of paint samples were performed in the QC laboratory of Kansai Plascon in Epping 2 Cape Town. The opacity of paint was determined by a sheen reflectometer (shown in Figure 3.6 below) and the gloss-meter (shown in Figure 3.7 below) was used to measure the gloss values of the film of paints.



Figure 3.6: Sheen reflectometer.



Figure 3.7: Sheen gloss meter

3.3. Methodology

3.3.1. Manufacturing of decorative water-based paint samples

All the experimental samples were prepared in 1 litre plastic containers, 11.5 cm in diameter and 12.3 cm height. The sample preparation followed the manufacturing process of water based paint in two stages (Youssef, 2019). In the dispersion stage, the pigment particles were wetted, dispersed and stabilised in an aqueous medium using high a speed mixer (Scholz et al., 2007). The second stage is called the 'finishing stage' or 'let down', during which the binder and most of the paint additives such as defoamer, coalescing agent, thickeners and fungicide were added to the product of the dispersion stage, also known as the mill-base (Youssef,

2019). In this study mixing speeds of the dispersion stage and the “let down” stage were 480 RPM and 120 RPM respectively.

The paint manufacture process is illustrated in the block flow diagram presented in Figure 3.8 below.

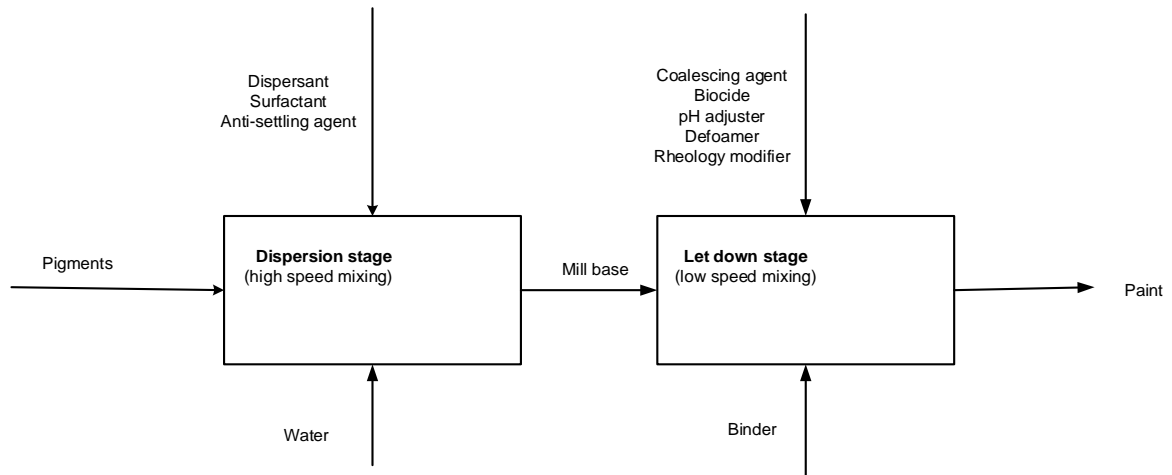


Figure 3.8: Paint manufacturing process

The product from the dispersion stage called the mill-base is a thick homogenous mixture (paste) while the product from the let-down is a homogeneous mixture with improved flow properties.

3.3.2. Research design

For each type of binder (i.e., pure acrylic and styrene acrylic binder), samples thickened with HEUR and HASE rheology modifiers were prepared. The concentration of the rheology modifier varied from 0 to 1.2 percent by weight (Auschra et al., 2015). In the sample preparation, only the concentration, the type of rheology modifier and the type of binder were varied. The concentration and type of the other raw materials were kept constant. The experiment design is given in Table 3.3 below.

Table 3.3: Experimental samples

Binder Type	Rheology Modifier type	Rheology modifiers concentration (%)	Sample number
Pure Acrylic	HEUR	0	1
		0.8	2
		1.2	3
	HASE	0	4
		0.8	5
		1.2	6
Styrene Acrylic	HEUR	0	7
		0.8	8

	1.2	9
HASE	0	10
	0.8	11
	1.2	12

3.4. Data production and analysis

3.4.1. Rheological tests

The rheological evaluation was performed by the Discovery Hybrid rheometer from TA instruments (shown in Figure 3.3), using a parallel plate measuring system with a 1 mm gape between the two plates.

The flow and deformation properties of the paint samples were measured by rotational and oscillatory tests. For each paint sample, the rheological tests were duplicated, and the final graphs were plotted from the averaged data collected.

The analysis of data obtained sought to correlate the rheological data to the paint properties. The rheological test conditions and specifications are discussed below.

The Viscosity curve test is a rotational test and can describe the effect of shear rate and shear stress on the viscosity of paint at a constant temperature of 25°C. The test was conducted by varying the shear rate from 10^{-3} to 10^3 s^{-1} , while the shear stress was varied from 1 to 1000 Pa.

The Dynamic amplitude sweep is an oscillatory test and illustrates how the loss and storage moduli change with increasing strain and gives an indication on the LVE region (Kästner, 2001; Mezger, 2006). This test was performed at a constant frequency of 1 Hz, a constant temperature of 25°C and a varied strain from 0.01% to 100%. The relationship between G' & G'' and strain under constant frequency and temperature was obtained.

The Frequency Sweep test is an oscillatory test that can evaluate the change in G' and G'' of paint when it is exposed to diverse time scale deformations (Overbeek et al., 2003). The Frequency Sweep Test in this study was performed under a constant strain of 0.1 percent, a fixed temperature of 25°C and under a frequency ranging from 0 to 100 rad/s.

The Three Interval Thixotropic Test (3ITT) consists of three intervals which include the low shear interval which simulates the structure of paint at rest, the high shear interval which describes the paint application process and the third interval at a low shear rate simulates the paint structure recovery over time (Moolman, 2003; Mezger, 2014). In this project, the first interval was performed in the oscillation mode at a frequency of 1Hz and a strain of 0.1 percent for a period of 60 minutes. The second interval was conducted in the rotational mode at a

shear rate of 1000 s^{-1} for a period of 120 minutes and the third interval was conducted under the same conditions as the first interval, but only for a period of 10 minutes.

3.4.2. Optical properties evaluation

Gloss and opacity are the optical properties of paint that were performed on the dry film of paint samples in this project.

Gloss: gloss was determined by applying a paint sample on a float glass, using a $200\mu\text{m}$ gape drawdown bar to ensure a uniform film thickness of $200 \mu\text{m}$. The applied film of paint was allowed to dry by placing the float glass in a 40°C oven for a period of one hour. The gloss measurements at 20° , 60° and 85° were determined using a gloss meter (shown in Figure 3.5).

Opacity: was determined by performing a contrast ratio (CR) test (Alua, 2012). This test consisted of applying paint of black and white card; also called a contrast ratio card using a $200\mu\text{m}$ gap drawn down bar to ensure uniform film thickness, using an automatic film applicator.

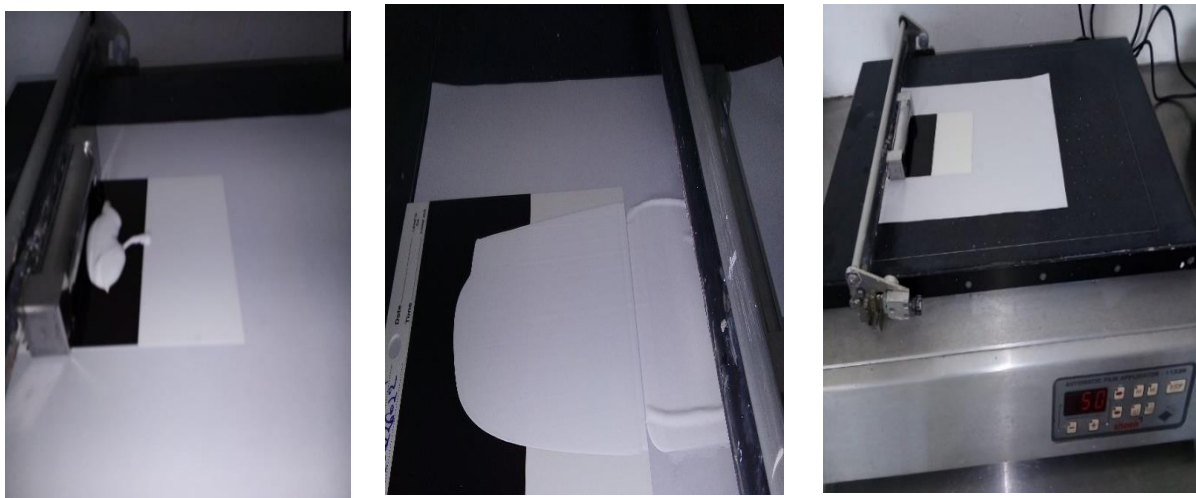


Figure 3.2: Contrast ratio test procedure

The film of paint was allowed to dry for 1 hour in a 40°C oven. The reflectance of the dry film of paint on the white and black parts of the contrast ratio card was measured using a sheen reflectometer (shown in Figure 3.7 above). The contrast ratio (CR) which is the reflectance on the black over the white substrate was then calculated using the following equation (Alua, 2012).

$$\text{CR} = \frac{\text{Reflectance on Black}}{\text{Reflectance on white}} \quad (3.10)$$

3.4.3. Mathematical Modelling

The mathematical modelling sought to obtain a model that described the flow curve data well, while using all the experimental paint samples. The mathematical models that were investigated are tabulated below.

Table 3.4: Mathematical models (Eley, 2019; Mezger, 2006; Moolman, 2003).

Models	Descriptions	Equations
Bingham	Fits paint with a yield point (Eley, 2006; Moolman, 2003).	$\sigma - \sigma_0 = \eta_p \dot{\gamma}$
Casson	Gives better representation of the yield point (Moolman, 2003).	$\sigma^{\frac{1}{2}} - \sigma_0^{\frac{1}{2}} = \eta_c^{\frac{1}{2}} \dot{\gamma}^{\frac{1}{2}}$
Power law	Suitable to describe the shear thinning behaviour at medium shear rates (Eley, 2006).	$\sigma = K\dot{\gamma}^n$
Herschel-Bulkley	The power law behaviour above the yield point (Eley, 2006).	$\sigma - \sigma_0 = K\dot{\gamma}^n$

3.4.4. Statistical analysis

The statistical analysis of rheological data from the flow curve test was performed by evaluating the coefficient of determination (R^2), the adjusted R^2 , the sum of squared error (SSE) and the root mean square errors (RMSE) of each of the models in table 3.4, using Microsoft Excel.

The coefficient of correlation R^2 was obtained from Ms Excel, by plotting the experimental results from the flow curve with each of the rheological models.

The adjusted R^2 was calculated using the following equation (Chai & Draxler, 2014; Pham, 2019):

$$R_{adj}^2 = 1 - \left(\frac{n-1}{n-k} \right) (1 - R^2) \quad (3.11)$$

The SSE was evaluated by applying the following formula (Chai & Draxler, 2014; Pham, 2019):

$$SSE = \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n-k} \quad (3.12)$$

The RMSE was determined based on the following expression (Chai & Draxler, 2014; Sutherland et al., 2014; Pham, 2019):

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{n-k}} \quad (3.13)$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Introduction

This chapter provides a discussion of the rheological and optical characteristics results of the twelve samples of white water-based paints, prepared as described in chapter three. The paint samples were subdivided in two groups; namely samples made of pure acrylic (PA) binder and samples made of styrene acrylic (SA) binder. For each group of experimental samples, the type and concentration of the rheology modifier were varied. The performance of HEUR and HASE rheology modifiers was evaluated in this research using the principles of rheology. Rheological tests included a flow curve, an amplitude sweep, a frequency sweep and 3ITT. Gloss and opacity or hiding power were the two optical properties studied on the experimental paint samples. The discussion of the flow curve test results and the modelling of data from the flow curve test are given in section 4.2 and 4.3, respectively. Section 4.4 deals with the analysis of the dynamic amplitude sweep test results. The discussion of the three interval thixotropy test and dynamic frequency sweep test results are provided in sections 4.5 and 4.6, respectively. Finally, the optical properties results are discussed in section 4.7.

4.2. Flow curves

The results of the viscosity curve test of paints containing HEUR and HASE rheology modifiers in the presence of a pure acrylic binder are given in Figure 4.8 below.

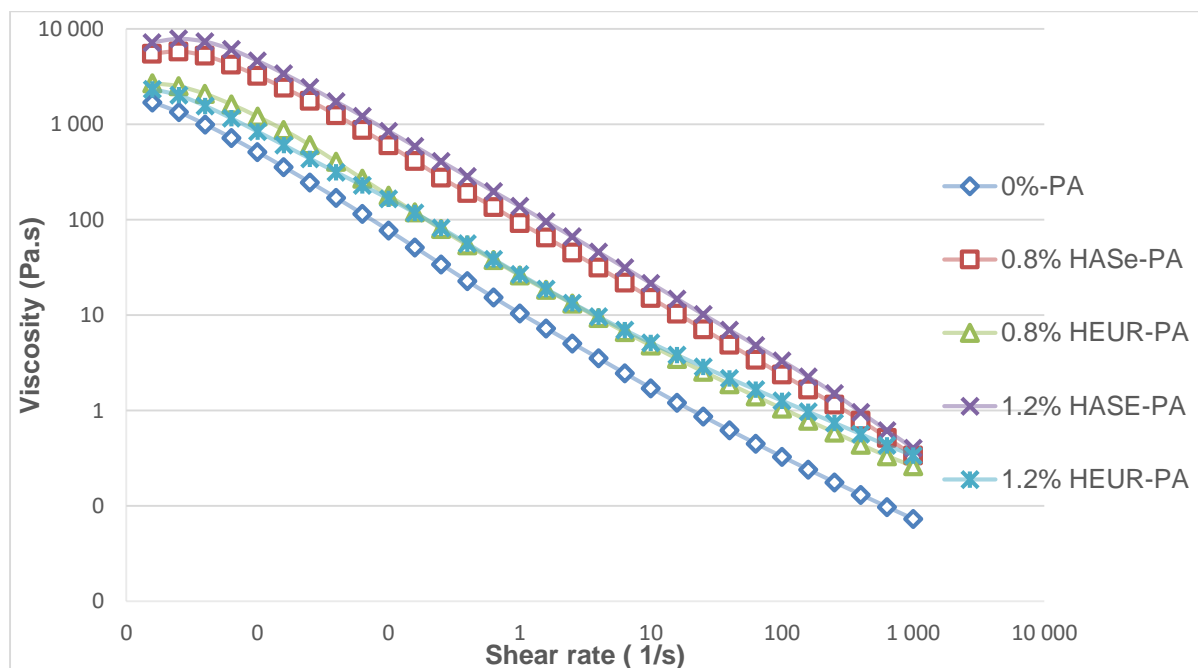


Figure 4.3: Viscosity curves results of paint samples made with pure acrylic binder.

Figure 4.8 illustrates the viscosity curves of sample of water-based paints containing pure acrylic binder and thickened by HEUR and HASE. All the samples of water paints were observed to be shear thinning, irrespective of the thickener used. These results are in agreement with Overbeek et al. (2003). The Results in Figure 4.8 show that a higher concentration of a HASE rheology modifier resulted in higher viscosities. Emélie et al. (1997) and Bhavsar & Shreepathi (2016) also found that the thickener type and concentration hugely affected the viscosity of water based paints.

The highest viscosity was observed in the formulation containing 1.2 percent of HASE; followed by the 0.8 percent HASE thickener. The reason for obtaining a higher viscosity with HASE than with the HEUR thickener could be linked to the composition and the thickening mechanism of this type of thickener (Kästner, 2001). The HASE rheology modifiers thicken water based paints by volume exclusion; resulting from neutralization of their carboxyl parts at a pH above 8 and by hydrophobic association (Kästner, 2001; Quadrat et al., 2001; de Souza et al., 2017). By contrast, the HEUR rheology modifiers thickening mechanism was entirely due to the adsorption of hydrophobic segments of the thickener onto the binder particles (Kästner, 2001; Quadrat et al., 2001; Xu et al., 2016). At any given shear rate, viscosities of HASE were higher than with a HEUR rheology modifier. For instance, at a low shear rate of 0.01s^{-1} paint sample with 0.8 percent HASE and 1.2 percent HASE had viscosities of 3.2×10^3 Pa.s and 4.6×10^3 Pa.s respectively. At the same shear rate 0.8 percent HEUR produced a viscosity of 1.2×10^3 Pa.s and a viscosity of 0.8×10^3 Pa.s was recorded for 1.2 percent HEUR. The higher viscosity produced by HASE thickener was advantageous for the storage stability but presented disadvantages during and after applications of water-based paints. High viscosity in the low shear rate range is advantageous because it prevent pigments from settling and instabilities during storage (Kästner, 2001). At the medium shear rate (250 s^{-1}), the sample thickened with 0.8 percent HASE and 1.2 percent HASE produced viscosities of 1.16 Pa.s and 1.51 Pa.s, respectively; 0.8 percent HEUR was found to have a viscosity of 0.58 Pa.s and the sample with 1.2 percent HEUR had a viscosity of 0.74 Pa.s. Higher viscosity in the medium shear range region can negatively affect the pumping and dispensing during the manufacturing of paints (Moolman, 2008) but also presents an advantage of easy transfer of paint to the brush or roller during application (Moolman, 2008). At the shear rate (10^3 s^{-1}), viscosities of 0.33 Pa.s and 0.40 Pa.s were recorded for 0.8 percent HASE and 1.2 percent HASE respectively, and 0.26 Pa. s and 0.33 Pa.s for paints with 0.8 percent HEUR and 1.2 percent HEUR respectively. Moolman (2008) reported that greater viscosity in the high shear rate region can lead to an adequate film thickness and better hiding power. The reason HEUR thickener offers lower viscosity at high shear rates is because the network formed after thickening with HEUR can easily be destroyed at high shear rates (Kästner, 2001) hence paint

thickened with HEUR offers an advantage of ease of application and good levelling after application.

Paint sample with 1.2 percent HEUR thickener have higher viscosity than those with 0.8 percent HEUR in the high shear rate region, whereas the opposite is observed in the low shear rate region. This higher viscosity of 1.2 percent HEUR than 0.8 percent HEUR under high shear rate conditions can be explained by the formation of hydrogen bonds, resulting from the interaction between HEUR's urethanes groups and the surfactant present in the paint formulation (Knoef, 1992). These hydrogen bonds can withstand high shear conditions. At higher HEUR concentrations (i.e., 1.2 percent) there are more hydrogen bonds formed, subsequent to higher viscosity in the high shear rates than with a 0.8 percent HEUR. The reason for the decrease of low shear viscosity as the HEUR thickener concentration increases could be explained by the weak hydrophobic groups of HEUR thickener; thus resulting in poor association and a decrease of viscosity in the low shear range (Moolman, 2003). This suggested that although higher HEUR concentrations are beneficial to flow and levelling properties after paint application, they can present poor storage stability properties, due to lower viscosity at low shear rates.

Figure 4.9 below shows the viscosity curve results of paints containing HEUR and HASE rheology modifiers, in the presence of a styrene acrylic binder.

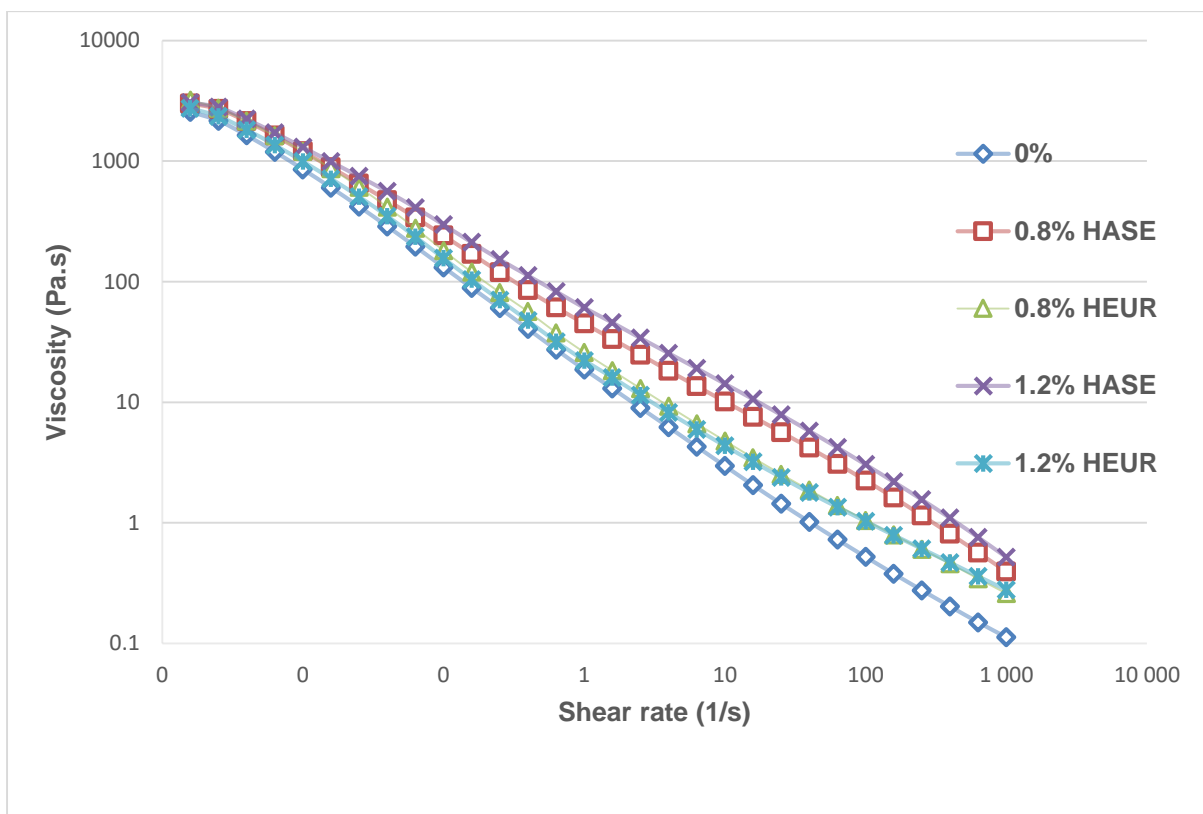


Figure 4.4: Flow curve results of paint samples made with styrene acrylic binder.

In Figure 4.9, the viscosity curves of different samples of paint thickened by HASE and HEUR rheology modifiers in the presence of styrene acrylic (SA) binder are shown. Similar to paint samples containing acrylic binder (Figure 4.8), all samples made with a styrene binder were determined to be shear thinning i.e., there is a decrease in viscosity as the shear rate increases. The thickening efficiency of HASE rheology modifier was found to be weaker in the presence of SA binder than with the PA acrylic binder.

Figure 4.9 shows that viscosities of formulation containing rheology modifiers are not far from the viscosity of the paint with no thickener (0 percent); and at any given shear rate, paint made with PA binder and HASE possess higher viscosities than SA paints.

For instance, at a shear rate of 0.01s^{-1} , in the presence of PA binder, the paint viscosities of 0.8 percent HASE and 1.2 percent HASE were found to be 3.2×10^3 Pa.s and 4.6×10^3 Pa.s respectively. In the presence of an SA binder, the paint viscosities of 0.8 percent HASE and 1.2 percent HASE were found to be 1.2×10^3 Pa.s and 1.3×10^3 Pa.s respectively. This weaker thickening efficiency of HASE rheology modifiers in the presence of an SA binder is mostly pronounced at low shear rates.

The highest viscosity was observed in the formulation thickened by 1.2 percent HASE followed by the viscosity of the paint containing 0.8 percent HASE throughout the shear range. In contrast, the performance of HEUR rheology modifier in the presence of PA and SA binder was found to be almost comparable in the low, medium and high shear rate ranges. For example, at low shear rate of 0.01s^{-1} in the presence of acrylic binder, the paint viscosities containing 0.8 percent HEUR and 1.2 percent HEUR were found to be 1.2×10^3 Pa.s and 0.8×10^3 Pa.s respectively. In the presence of SA binder 0.8 percent HEUR and 1.2 percent HEUR produced paint viscosities of be 1.1×10^3 Pa.s and 0.9×10^3 Pa.s respectively.

At a mid-shear rate of 250 s^{-1} at 0.8 percent HEUR rheology modifier, the viscosity of paints based of PA binder and SA binder was found to be 0.58 Pa.s and 0.6 Pa.s. Furthermore, at a high shear rate of 10^3s^{-1} , paints made of PA and SA binders at 0.8 percent HEUR were found to have an identical viscosity of 0.26 Pa.s; at 1.2wt. percent HEUR, A sample containing pure acrylic had a slightly higher viscosity (0.33 Pa.s) than a styrene acrylic binder (0.277 Pa.s).

4.2.1. Effect of binder type on the performance of a HASE rheology modifier

Figure 4.10 below comprises the flow curve results of paint samples containing 0.8 percent and 1.2 percent HASE rheology modifiers in the presence of pure acrylic; as well as a styrene acrylic binder.

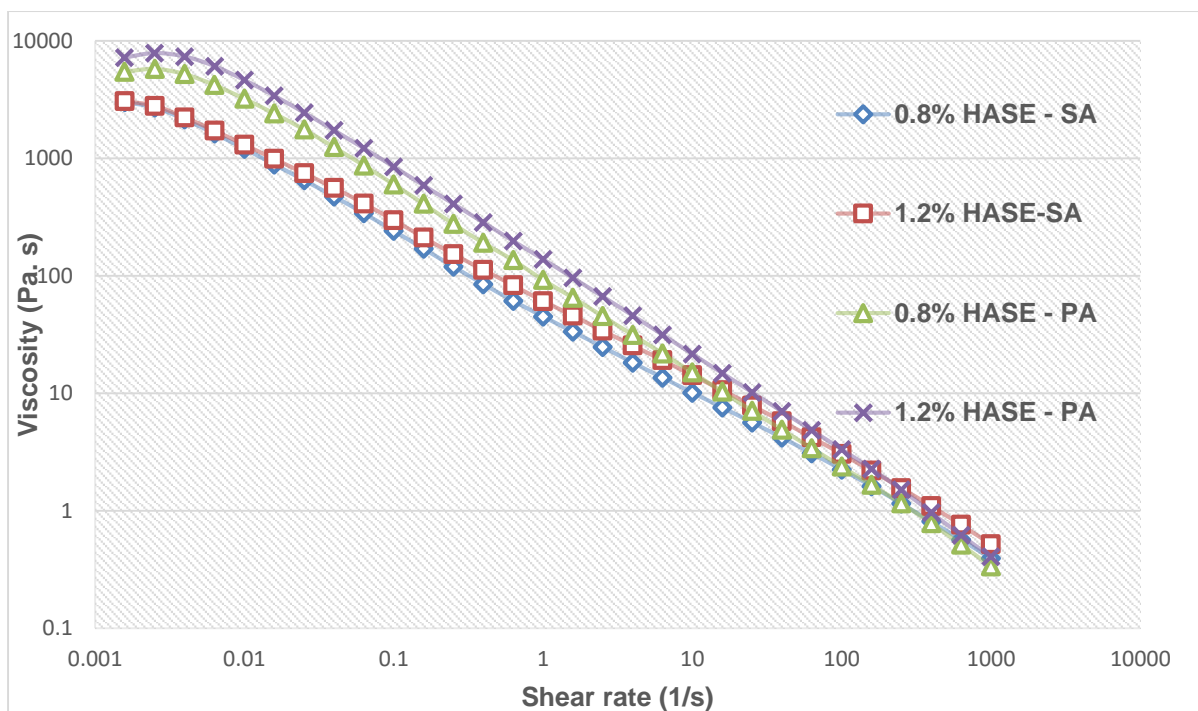


Figure 4.5: Performance of HASE rheology modifier in the presence of pure and styrene acrylic binders

Paint samples thickened by 0.8 percent HASE and 1.2 percent HASE thickener concentrations in the presence of a PA binder were found to produce higher viscosities in the low and medium shear rates than with a HASE thickener in the presence of SA binder at the same concentrations. For instance, at a low shear rate of 0.01s^{-1} , 0.8 percent the HASE in the presence of pure acrylic produced a viscosity which was 2.6 times larger than the viscosity of 0.8 percent the HASE in the presence of an SA binder. Also, the viscosity at a 1.2 percent HASE concentration in the presence of a PA binder was obtained to be 3.5 times higher than 1.2 percent HASE in the SA binder at shear rate 0.01s^{-1} .

Furthermore, the poor thickening efficiency of HASE rheology modifiers in the formulation containing a styrene binder is due to the high hydrophobicity of styrene (Šňupárek et al., 2005). This hydrophobicity of the SA binder hinders the swelling of binder particles with a pH above 8 by preventing the binder particles from neutralizing their carboxylic groups (Šňupárek & Quadrat, 2006; Fardi et al., 2018). The higher thickening viscosity of HASE in the presence of an PA binder could be linked to the smaller particle size and relatively low hydrophobicity of pure acrylic binders (Glass & Prud'homme, 1997; Polverejan, 2017). The smaller particle size provides a larger surface area and greater contact with HASE thickener particles (Polverejan, 2017; El-wahab et al., 2018) and the lower hydrophobicity makes it possible for the carboxylic groups contained in the PA binder particles to be neutralized by the thickener at a pH above 8, resulting in like charges to repel the swelling of the polymer (Glass, 1999).

Although the viscosities of the formulations of the two binders differs in the low and medium shear rates at each concentration, their viscosities are comparable in the high shear rates region. For instance, at a shear rate of 10^3s^{-1} in the presence of a PA binder, the viscosity of paint with 0.8 percent HASE and 1.2 percent HASE were found to be 0.33 Pa.s and 0.40 Pa.s, respectively. in the presence of the SA binder their viscosities were determined to be 0.40 Pa.s and 0.52 Pa.s respectively. This finding comes with agreements with Glass (1999) who reported that the viscosity of water based paint in the high shear rate is not affected by the binder particle size. The difference in viscosities in the low and medium shear rates implies that these paints will behave differently while in storage compared to their behaviour when exposed to medium shear rates. For instance, lower viscosities at a lower shear rate will lead to pigment settling and instabilities during storage (Kästner, 2001).

4.2.2. Effect of binder type on the performance of HEUR rheology modifier.

Figure 4.11 below shows the performance of a HEUR rheology modifier in the presence of a pure acrylic and styrene binder.

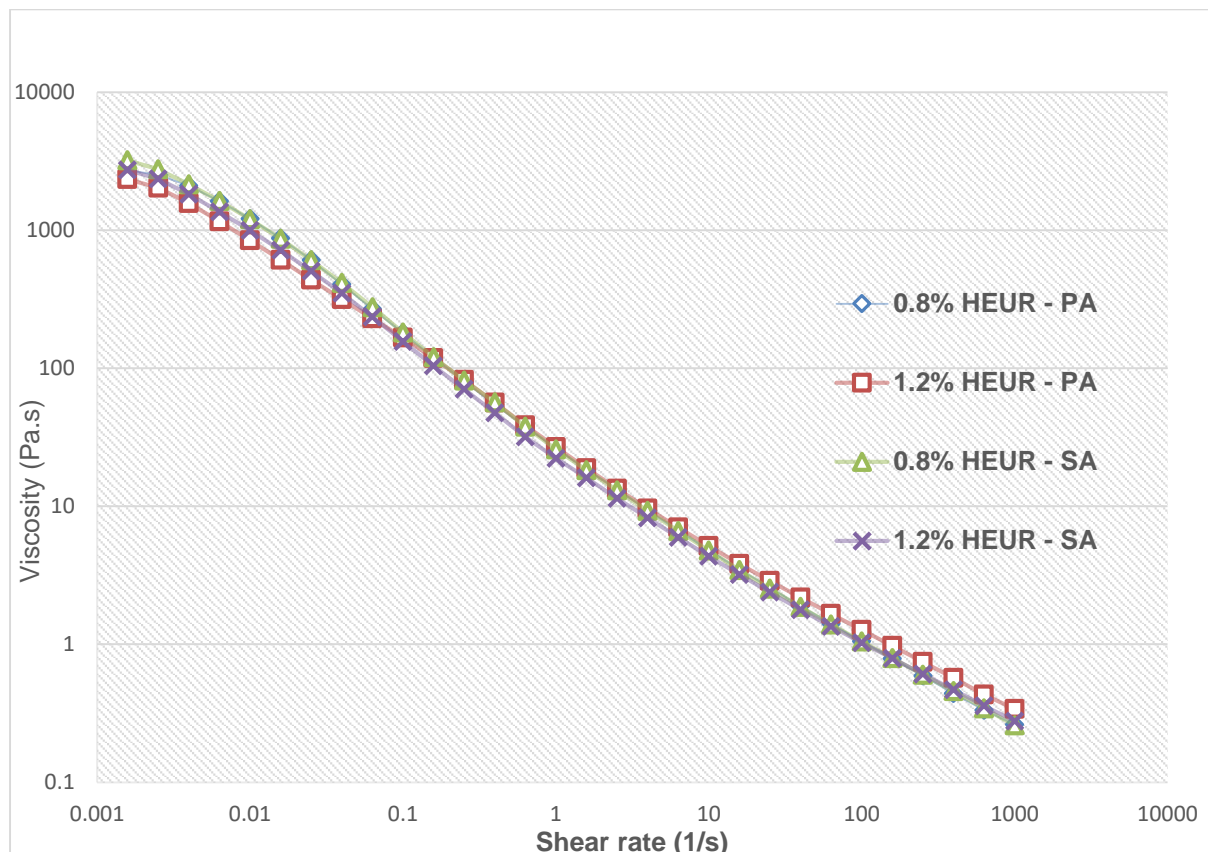


Figure 4.6: Performance of HEUR rheology modifiers in the presence of pure and styrene acrylic binders.

The results shown in Figure 4.11 demonstrate that the performance of a HEUR rheology is not dependent on the type of binder as there is an insignificant difference in viscosity at any

given shear rate. For instance, at a low shear of 0.01s^{-1} , samples with 0.8 percent HEUR were found to have viscosities of $1.2 \times 10^3 \text{ Pa}\cdot\text{s}$ and $1.1 \times 10^3 \text{ Pa}\cdot\text{s}$ for PA and SA binder, respectively. At a mid-shear rate of 250 s^{-1} , 0.8 percent HEUR produced viscosities of $0.58 \text{ Pa}\cdot\text{s}$ and $0.60 \text{ Pa}\cdot\text{s}$ for paints with PA binders and SA binders, respectively. The reason for this finding could be ascribed to the fact that, unlike HASE thickener, A HEUR thickener is made of weaker hydrophobic moieties. The thickening by a HEUR thickener is principally a result of hydrophobic interaction with the binder particles; hence with HEUR there is constrained association with binder particles (Auschra et al., 2015). The results presented in Figure 4.11 show that for both binders, the increase in HEUR concentration results in lower viscosity at low shear but the opposite is observed at high shear rates. Moolman (2003) also observed similar findings. For instance, paint with 1.2 percent HEUR in the presence of a pure acrylic binder has the lowest viscosity in the low shear region but possesses the highest viscosity under high shear conditions. This could be attributed to the higher hydrophobicity of styrene binders (Auschra et al., 2015) as well as a stronger crosslink between the hydrophobic end-groups of the thickener and binder particles (Huldén, 1994).

Eley (2019) demonstrated that shear rate is not the controlling parameter of paint flow because it is dependent of the paint's rheology. Shear stress, on another hand, is independent of rheology. Paint application, as well as post application processes such as brushing, sagging and levelling are controlled by the shear stress (Eley, 2019). Therefore, the viscosity-shear stress plot is more suitable for the flow analysis of paints than for viscosity-shear rate (Eley, 2019; Gaggero et al., 2021). The flow curve data expressing the viscosity in function of shear stress, measured in Controlled Shear Rate (CSR) mode are given in Figures 4.12 and 4.13.

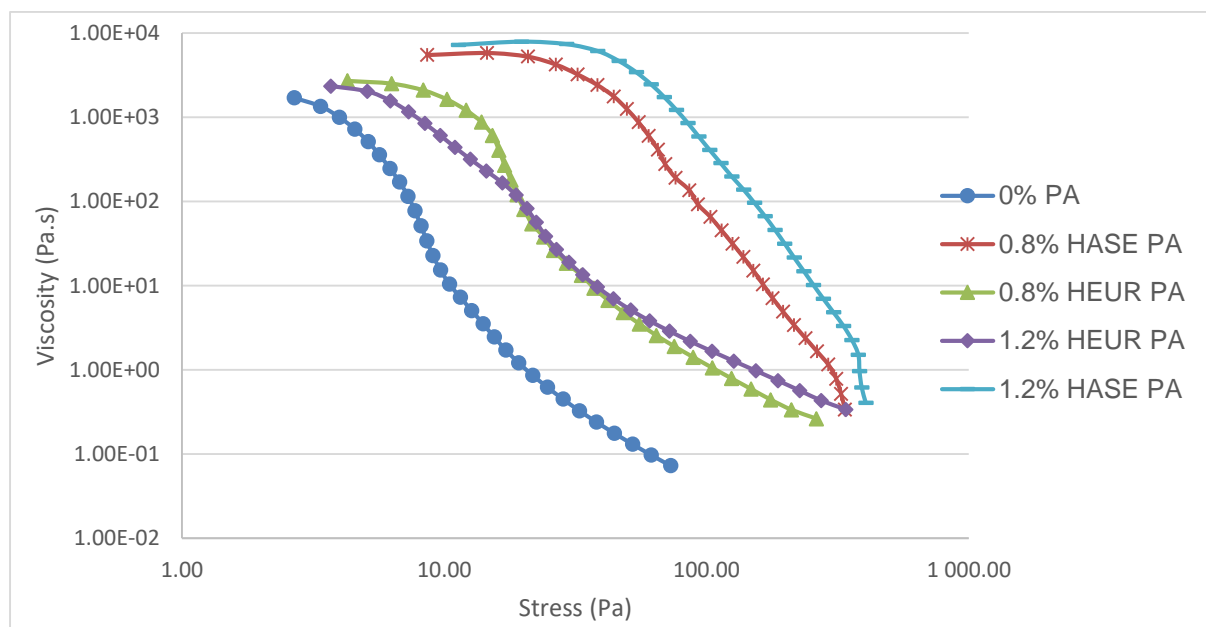


Figure 4.7: Viscosity-shear stress plot of paints based on PA binder.

In Figure 4.12, the viscosity is measured as a function of shear stress under the CSR mode of paint, thickened with HASE and HEUR, in the presence of a PA binder. Gaggero et al. (2021) also reported viscosity in function to shear stress in a CSR, to study the rheology of paint. Just as for the viscosity-shear rate plots, the shear thinning character of paint samples can be observed as the viscosity was found to be decreasing with increasing shear stress. The viscosity was observed to increase with HASE concentration, at any given shear stress level. In the case of HEUR, the viscosity in the low shear stress was found to be decreasing with increasing thickener concentration and at higher shear stress, the viscosity was observed to be increasing with increased thickener concentration. The performance of 0.8 percent HEUR and 1.2 percent HEUR was found to be similar in the mid-shear stress range. The viscosity in low shear rate, as well the low shear stress represents the storage stability by considering the plateau (Gaggero et al., 2021).

The results presented in Figure 4.12 reveal that the viscosity at low shear stress best represents the properties of paint at rest. For instance, it can be observed that paint samples with HASE thickener do not only possess the highest viscosity but also display a plateau at low shear stress. This confirms the results obtained from the viscosity-shear rate plots that HASE imparts a better anti-settling property to paint than HEUR. Paints with HEUR thickener do not display a plateau in the low shear region. High HEUR concentration can be detrimental to storage stability because it decreases the low shear viscosity but also displays a stepped decrease in viscosity as the shear stress is increased. Considering the plateau, as far as sagging and levelling properties are concerned, HASE will have poor levelling properties, but will offer good sag resistance (Eley, 2019).

Gaggero et al. (2021) utilised the data from the viscosity shear stress plot in CSR mode, to measure the yield stress of paint. Similarly, in this work the yield stress was determined from the viscosity shear stress graph presented in Figures 4.12 and 4.13, as the point of intersection of the tangent at the beginning of the viscosity drop differs from the almost linear segment, at low shear stress (Gaggero et al., 2021). The results of yield stress paint samples made of PA binder as well as SA binders at different thickener concentrations are presented in Table 4.5 below. In the presence of pure PA binder, paint thickened with HASE thickener was found to have higher yield stress values than HEUR. The yield stress was found to be increasing along with the increase of HASE concentration, but the opposite trend was observed for the HEUR rheology modifier. For instance, yield stress of 32 Pa and 54 Pa was recorded for the paint with 0.8 percent HASE and 1.2 percent HASE respectively. In the case of HEUR, the yield stress dropped from 12 Pa to 6 Pa, as the thickener concentration increased from 0.8 percent to 1.2 percent.

The presence of yield stress presents both advantages and disadvantages for structured materials such as paints (Eley, 2019). Some advantages of the presence of yield stress include the improvement of the storage stability by preventing flocculation and sedimentation (Eley, 2019). The presence of the yield stress can present disadvantages during the manufacturing process of paint, such as inadequate pumpability and poor mixing properties (Eley, 2019). Therefore, linking the yield stress results to the performance of water-based paints, it can be deduced that paint containing HASE in the presence of PA binder is expected to have good storage stability but will present difficulties during manufacturing due to poor pumping and mixing properties. On the other hand, HEUR thickener is expected to suffer irregularities while in storage (Reuvers, 1999).

Table 4.5: Yield stress results from viscosity-shear stress plot.

Yield stress (Pa)		
	PA Binder	SA Binder
0%	2.6	4.00
0.8% HEUR	12	4.09
0.8% HASE	32	4.75
1.2% HEUR	6	4.32
1.2% HASE	54	4.84

The viscosity curve data in function of shear stress of paints made of SA binder are illustrated in Figure 4.13 below

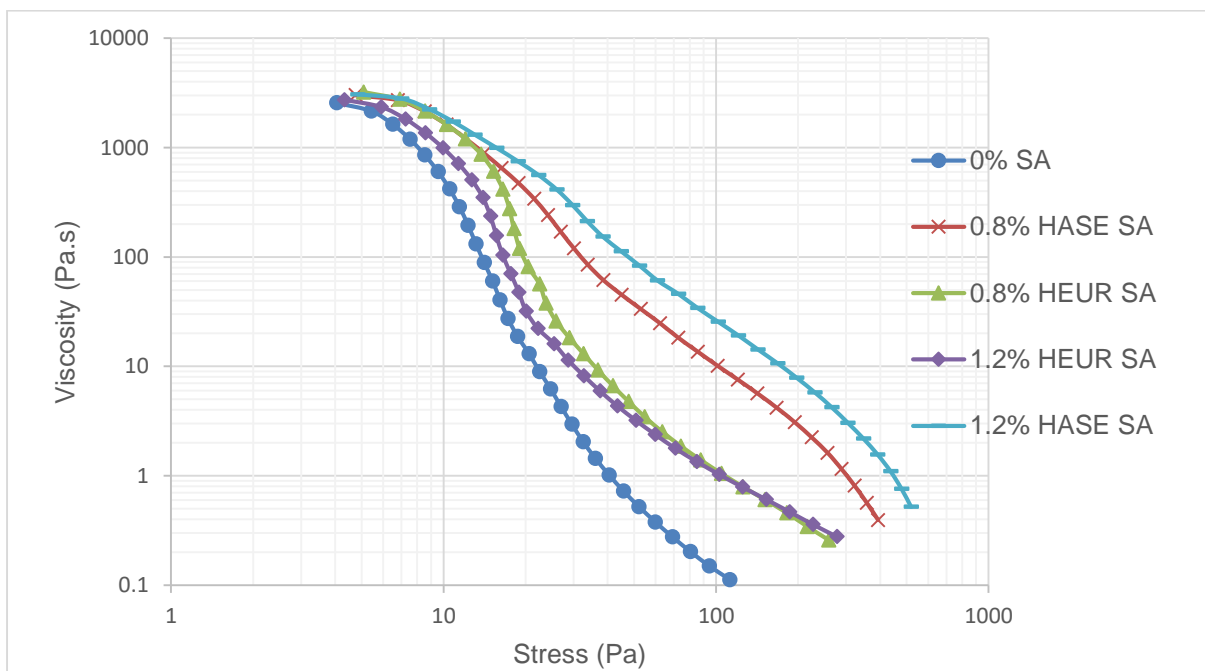


Figure 4.8: Viscosity-shear stress plot of paints based on SA binder.

The viscosity data of paints thickened by HASE and HEUR in the presence of an SA binder, while dealing with the shear stress in CSR mode are presented in Figure 4.13. What is analogous for paints made of PA binder, is that paint containing SA binder were observed to be shear-thinning, regardless of the type and the concentration of thickener used. Paint samples made using an SA binder do not display a plateau in the low shear stress range. This finding suggests that these two groups of paints behave differently while in storage (Gaggero et al., 2021). When comparing the yield stress results of paints containing PA and SA binder in Table 4.5. it was observed that paints with a PA binder produced higher yield stress values than those with an SA binder for all experimental samples except for samples with 0 percent thickener concentration. The reason for such finding could be ascribed to the fact that the PA and SA binders have different chemical compositions and different particle sizes and that the thickening mechanism associative rheology modifier is therefore affected by the type of binder in formulation (Fardi et al., 2018). The relatively low yield stress value for samples made with an SA binder suggests that irrespective of the type of thickener used, these paints will possess irregularities while in storage such as sedimentation and flocculation (Eley, 2019).

4.3. Modelling of rheological data.

This section will discuss how data from the flow curve test shown in Figures 4.8 to 4.11 fitted the rheological models used for flow analysis. The Power Law, Bingham, Casson and the Herschel-Bulkley models will be utilised in the study. Furthermore, statistical analysis was performed to determine which model provided the best fit for the experimental results. The statistical parameters that were used to evaluate data fitting included the coefficient of determination (R^2), the adjusted R^2 , the sum of squares error (SSE) and the root mean square error (RMSE).

4.3.1. Power law

The flow parameters and statistical analysis from the Power Law fit of paint samples made of pure acrylic binder are given in Table 4.6 below.

Table 4.6: Power Law parameters for paint samples containing pure acrylic binder

Thickener type and concentration	n	K(Pa.s ⁿ)	R ²	Adjusted R ²	SSE	RMSE
0%	0.2254	11.905	0.9701	0.9691	502	4
0.8% wt. HEUR	0.2745	30.369	0.9553	0.9553	5797	14
0.8% wt. HASE	0.2531	81.077	0.9107	0.9076	33068	33
1.2% wt. HEUR	0.3144	30.120	0.9830	0.9824	36783	34.4
1.2% wt. HASE	0.2499	112.66	0.8836	0.8796	111103	60

The Power Law parameters and the statistical analysis for paint samples formulated with SA binder are tabulated in Table 4.7 below.

Table 4.7: Power Law parameters for paint samples containing styrene acrylic binder

Thickener type and concentration	N	K(Pa.s ⁿ)	R ²	Adjusted R ²	SSE	RMSE
0%	0.2285	19.533	0.9492	0.9474	134	2
0.8% wt. HEUR	0.2658	31.092	0.9667	0.9656	7875	16
0.8% wt. HASE	0.3316	46.940	0.9841	0.9835	7417	15
1.2%wt. HEUR	0.2840	27.834	0.9646	0.9634	11510	19
1.2% wt. HASE	0.3531	59.440	0.9860	0.9855	40399	36

The power Law parameters include the flow index (n) which indicated the extent of shear thinning and consistency index (K) which provided an indication on the viscosity at low shear condition (Adewale et al., 2017).

The flow indices (n values) of the samples were found to be less than one. Values below one mean that the experimental paint samples are pseudoplastic i.e. shear thinning (Moolman, 2003; Eley, 2019). This finding confirmed the flow curve results shown in Figures 4.8 and 4.9 where the viscosity decreased with increasing shear rate. The highest flow index was found to be 0.3531 in the sample of paint thickened with by 1.2 percent HASE rheology modifiers in the presence of an SA binder. The lowest flow indices were found to be 0.2285 in the samples without thickener which are comparable for both binders.

The low n values for samples without thickener indicated that their structures destroyed more at high shear rates than samples containing rheology modifier (Moolman, 2003). Although both binders have similar flow indices at a 0 percent thickener concentration, their consistency (K) values are different at 0 percent thickener concentration. For each binder, the lowest K value was found to be with samples without thickener and the highest K value was observed to be with sample containing 1.2 percent HASE thickener. The highest K was found to be 112.6 Pa.s ^{n} in the sample thickened with 1.2 percent HASE rheology modifier, in the presence of a PA binder. Comparing the K values and the viscosity results in Figure 4.8 and Figure 4.9, a relationship between low shear viscosity and the K consistency value can be established. For instance, for both binders, the paint samples with 1.2 percent HASE had the highest viscosities, followed by 0.8 percent HASE, then 1.2 percent HEUR and 0.8 percent HEUR and the lowest viscosity at 0 percent thickener. The K values followed the same trend. These

results are in agreement with Moolman (2003) who found similar results and established that n and K values can be used to evaluate the application properties and the storage stability of water based paints, respectively. Furthermore, the thickening efficiency of rheology modifiers can be effectively evaluated by the consistency index K . The higher the K value, the higher the thickening efficiency of the rheology modifier used. For example, HASE rheology modifier at a concentration of 1.2 percent in the presence of pure was found to have highest thickening efficiency, followed by 1.2 percent HASE in the presence styrene binder. The HEUR rheology modifier had a similar thickening efficiency in the presence of each binder as the K values of paints containing HEUR rheology modifier were comparable.

The paint samples that best fitted the power law equation are 1.2 percent HASE and 0.8 percent HASE in the presence of an SA binder and the sample thickened with 1.2 percent HEUR in the presence of SA binder, as they had the highest coefficient of determination, R^2 and adjusted R^2 . For all the experimental paint samples, the adjusted R^2 was determined to be slightly lower than R^2 . This proximity of R^2 and adjusted R^2 suggested that the number of independent variables of power law (n and K) had a minor effect on the regression model (Pham, 2019). A relationship between SSE and RMSE can be established for all the experimental paint samples as it can be observed that RMSE increases with increasing SSE values. The RMSE for the Power law data was found to vary between 4 and 60 for the samples using the PA binder and between 2 and 36 for paint samples using the SA binder.

For both binders, the lowest RMSE was found to be with the data produced by the sample with the lowest viscosity i.e., 0 percent rheology modifier, while the highest RMSE was observed with the paint with the highest viscosity (1.2 percent HASE). As the RMSE value represented the degree of deviation between the experimental and the model fitted data (Chai & Draxler, 2014; Pham, 2019); it can be proposed that there is more deviation from the empirical data as the paint viscosity increases. For example, the RMSE values of paint samples made with a styrene binder were observed to be lower than paint samples with a pure acrylic binder. This is because samples made with SA binder (specially containing HASE) are lower in viscosity than the ones formulated with a PA binder. Burari, et al., (2010) reported that RMSE values of less than 50 are acceptable. Therefore, Power Law describes the experimental data as showing that 90% of the RMSE values for this model were below 50.

4.3.2 Bingham equation

Table 4.8 below encompasses the Bingham parameters i.e., plastic viscosity (n_p) and the yield point (σ_0), as well as the statistical analysis parameters of paint samples that contain pure acrylic binder.

Table 4.8: Bingham parameters for paint samples made with pure acrylic binder

Thickener type and concentration	η_p	$\sigma_0(Pa)$	R^2	Adjusted R^2	SSE	RMSE
0%	0.0755	11.727	0.8135	0.8071	1859	8
0.8 wt. % HEUR	0.2762	31.832	0.8487	0.8487	19374	24
0.8 wt. % HASE	0.3491	95.259	0.5614	0.5414	135677	66
1.2 wt. % HEUR	0.3663	33.778	0.8646	0.8599	29940	31
1.2 wt. % HASE	0.4011	136.32	0.4616	0.4616	267325	93

The Bingham model parameters as well as the statistical analysis of paint samples with SA binder are tabulated in Table 4.9 below.

Table 4.9: Bingham parameters for paint samples made with a styrene acrylic binder

Thickener type and concentration	η_p	$\sigma_0(Pa)$	R^2	Adjusted R^2	SSE	RMSE
0%	0.1139	19.699	0.7943	0.7872	134	2
0.8 wt. % HEUR	0.2777	32.020	0.8487	0.8487	19327	25
0.8 wt. % HASE	0.444	62.868	0.6900	0.6793	121232	63
1.2 wt. % HEUR	0.2988	28.970	0.8707	0.8662	18885	25
1.2 wt. % HASE	0.5930	85.489	0.6789	0.6678	1057314	185

Most experimental paint samples fitted well with the Bingham model as the R^2 varied from 0.46 to 0.84. Henseler et al. (2009) suggested that the R^2 threshold of a good fit is in the range of 0.75 and 1. For both binders, the highest and lowest plastic viscosity were found in the paint sample at 1.2 percent HASE and 0 percent thickener concentrations, respectively. Similarly, the highest and the lowest yield stress for this model were found at 1.2 percent HASE and 0 percent thickener concentrations, respectively for both binders. The highest yield stress for this model was found to be 136.32 Pa in the paint sample thickened with 1.2 percent HASE thickener, in the presence of PA binder followed by the sample of 0.8 percent HASE in the presence of PA binder, which has a yield stress of 95.259 Pa. The yield stress obtained from the Bingham model was found to be dependent on the thickener type and concentration. It can be observed that the yield stress increases as the thickener concentration increases. It was also observed that paint samples containing HASE rheology modifier produced greater yield stress than those containing HEUR. Furthermore, it was found that paints made with PA binder have higher yield stress than the samples made with styrene binder while the plastic viscosity seems to follow an opposite trend i.e., the plastic viscosity values are higher in

samples made with styrene acrylic binder. Similar to power law, the adjusted R^2 was found to be slightly lower than R^2 . In the case of statistical data produced by the Bingham model. The RMSE was found to vary between 8 and 93 for the samples made with pure acrylic binder and 2 to 185 for samples made with styrene acrylic. It has been established that RMSE and SSE increases with increasing plastic viscosity.

4.3.3. Casson's equation

The statistical analysis as well as the Casson's model parameters i.e., Casson viscosity and the yield stress of paint samples made of pure acrylic binder are tabulated in Table 4.10 below.

Table 4.10: Casson's equation parameters for paint samples made with pure acrylic binder

Thickener type and concentration	η_c	$\sigma_0(Pa)$	R^2	Adjusted R^2	SSE	RMSE
0%	0.0484	7.642	0.8779	0.8731	4193	12
0.8% HEUR	0.1991	18.214	0.894	0.8903	40695	36
0.8% HASE	0.2267	61.856	0.6713	0.6599	213931	83
1.2% HEUR	0.2886	16.839	0.9066	0.9033	54859	42
1.2% HASE	0.2557	90.4097	0.5948	0.5808	627078	142

In Table 4.11 below, the statistical and Casson model parameters of paint samples made of styrene acrylic (SA) binder are tabulated.

Table 4.11: Casson's equation parameters for paint samples made with styrene acrylic binder

Thickener type and concentration	η_c	$\sigma_0(Pa)$	R^2	Adjusted R^2	SSE	RMSE
0%	0.071	13.074	0.8453	0.8400	10752	19
0.8% HEUR	0.2000	18.411	0.9014	0.898	12344	62
0.8% HASE	0.3700	30.361	0.8014	0.7945	173414	75
1.2% HEUR	0.2244	15.640	0.9182	0.9153	38961	34
1.2% HASE	0.5093	39.506	0.7831	0.7756	1057314	185

Most experimental paint samples fit well the Casson's equation as R^2 results vary from 0.59 to 0.91. The R^2 threshold of a good fit is should be in the range of 0.75 and 1 (Henseler et al., 2009). Paint samples thickened with HEUR rheology modifier in the presence of both binders

were found to produce better fits of Casson's equation because they have the highest values of R^2 and adjusted R^2 . The highest Casson viscosity was found to be 0.5093 in the paint containing 1.2 % HASE thickener in the presence of SA binder. The lowest Casson viscosity was found in the paint samples without a rheology modifier i.e., 0 percent. The highest Casson viscosity in the formulation with pure acrylic binder was obtained in the paint sample with 1.2 percent HEUR and for the SA binder the sample with a 1.2 percent HASE had the highest Casson viscosity. Similarly, to the Bingham model, the highest yield stress from the Casson equation was found in the presence of PA binder, in the samples thickened by a 1.2 percent HASE rheology modifier. With the HASE rheology modifier, the yield stress can be observed to be increasing as the rheology modifier concentration increases, but the opposite trend is observed for the HEUR rheology modifier in the presence of PA and SA binder.

The statistical results showed that the Casson model recorded the highest RMSE and SSE. The RMSE is in the range of 12 to 142 and 19 to 185 for formulations with pure acrylic and styrene acrylic respectively. A correlation between the yield stress of paint thickened with HASE rheology and the RMSE values was observed. The RMSE was observed to be increasing as the yield stress of paint containing HASE increased. It is worth noting that paint samples thickened with HASE rheology modifiers produced larger values of RMSE and SSE, which means greater deviations from empirical results. Furthermore, samples with the HASE rheology modifier were observed to have the lowest adjusted R^2 and the highest SSE and RMSE. This result suggests that paint samples thickened by HASE not only provided the worst fits for Casson model but also produced the highest deviations.

4.3.4. Herschel-Bulkley model

The statistical analysis and the Herschel-Bulkley parameters for paint samples made of pure acrylic binder are given in Table 4.12 below. The Herschel-Bulkley parameters include the yield stress (σ_0), the consistency (K) and the flow index (n).

Table 4.12: Herschel-Bulkley model parameters for paint samples made of pure acrylic binder

Thickener type and concentration	$\sigma_0(Pa)$	$K(Pa.s^n)$	n	R^2	Adjusted R^2	SS	RMSE
0%	4.12	5.63	0.359	0.9449	0.9410	31	1
0.8% HEUR	9.603	14.780	0.371	0.9479	0.9441	31	1
0.8% HASE	12	18.8	0.3885	0.9451	0.9411	157758	71
1.2% HEUR	7.718	16.169	0.375	0.9594	0.9565	219	3
1.2% HASE	16	26	0.391	0.9489	0.9453	273026	94

Table 4.13 below contains the statistical analysis and Herschel-Bulkley model parameters of paint samples made of styrene acrylic binder.

Table 4.13: Herschel-Bulkley model parameters for paint samples made of styrene acrylic binder

Thickener type and concentration	$\sigma_0(Pa)$	$K(Pa.s^n)$	n	R^2	Adjusted R^2	SS	RMSE
0%	6.443	10.53	0.328	0.9589	0.9559	134	2
0.8% HEUR	9.65	14.786	0.350	0.9519	0.9485	200	2.55
0.8% HASE	11.5	17	0.387	0.9428	0.9387	134807	66
1.2% HEUR	8.69	12.253	0.360	0.9468	0.9430	160	4
1.2% HASE	15.5	19.1	0.389	0.9336	0.9290	860916	166

Tables 4.13 shows that flow curves data of all experimental paint samples fits the Herschel-Bulkley model well, as the R^2 and adjusted R^2 values vary between 0.93 and 0.96. This observation is in agreement with Eley (2019) who reported that Herschel-Bulkley fits effectively with numerous types of paints. The Herschel-Bulkley model's parameters tabulated in Table 4.12 and Table 4.13 describe certain flow properties of water-based paints. For instance, the shear thinning behaviour of all experimental samples is established as all n values were found to be less than one (Eley, 2019). Comparing the n values generated by the power Law to the n values from the Herschel-Bulkley equation, it can be observed that the later model produced higher n values than the Power Law.

The higher values of the flow indices from the Herschel-Bulkley equation could be ascribed to the fact that power law does not consider the yield stress while the Herschel-Bulkley model considers the yield stress. Like Bingham and Casson models, the yield stress from the Herschel-Bulkley was found to be dependent on the type of binder, type of thickener and the concentration of the thickener. The reason for this finding could be attributed to the difference in thickening mechanisms between HASE and HEUR rheology modifiers and the effect of the binder type on their thickening mechanisms.

The statistical results showed that the Herschel-Bulkley model produced the lowest RMSE, compared to other models. For instance, in the presence of the PA binder, an RMSE of 1 was obtained for the sample with 0 percent and the sample with 0.8 percent HEUR, while the sample with 1.2 percent HEUR recorded an RMSE of 3. In the presence of the SA binder, the

sample with 0 percent, 0.8 percent HEUR and 1.2 percent HEUR had a, RMSE of 2, 3 and 4 respectively.

It is worth noting that paint without a rheology modifier of 0% and the ones with HEUR rheology modifiers have the highest adjusted R^2 and the smallest RMSE and SSE values. Power law and Herschel-Bulkley were found to be the best models as they generated smaller values of RMSE and larger adjusted R^2 and R^2 (Pham, 2019). Sutherland et al.(2014) also used adjusted R^2 and RMSE to confirm that Power Law and Herschel-Bulkley fitted well the rheological data of a structured fluid well.

4.4. Dynamic amplitude sweep

As described in chapter three, the Dynamic Sweep test measures storage modulus (G') and the loss modulus (G'') with increasing strain. The strain was varied from 0.01 to 100%, at a constant temperature of 25°C. Figure 4.14 and Figure 4.15 illustrate the dynamic amplitude sweep results of paint formulation thickened with HASE and HEUR rheology modifiers at different concentrations, in the presence of a pure acrylic (PA) binder.

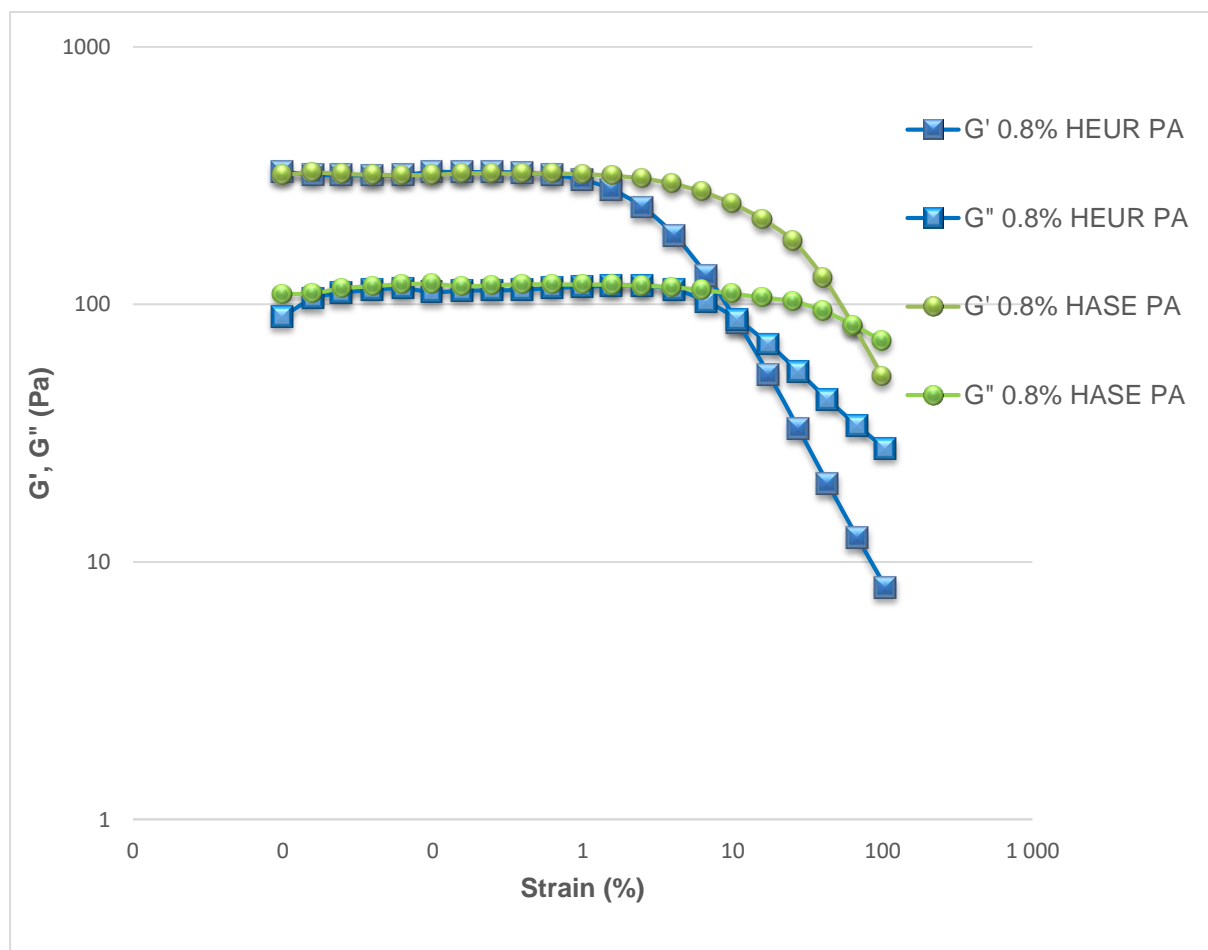


Figure 4.9: Amplitude sweep test results for paints containing 0.8% of HEUR and HASE in presence of pure acrylic (PA) binder.

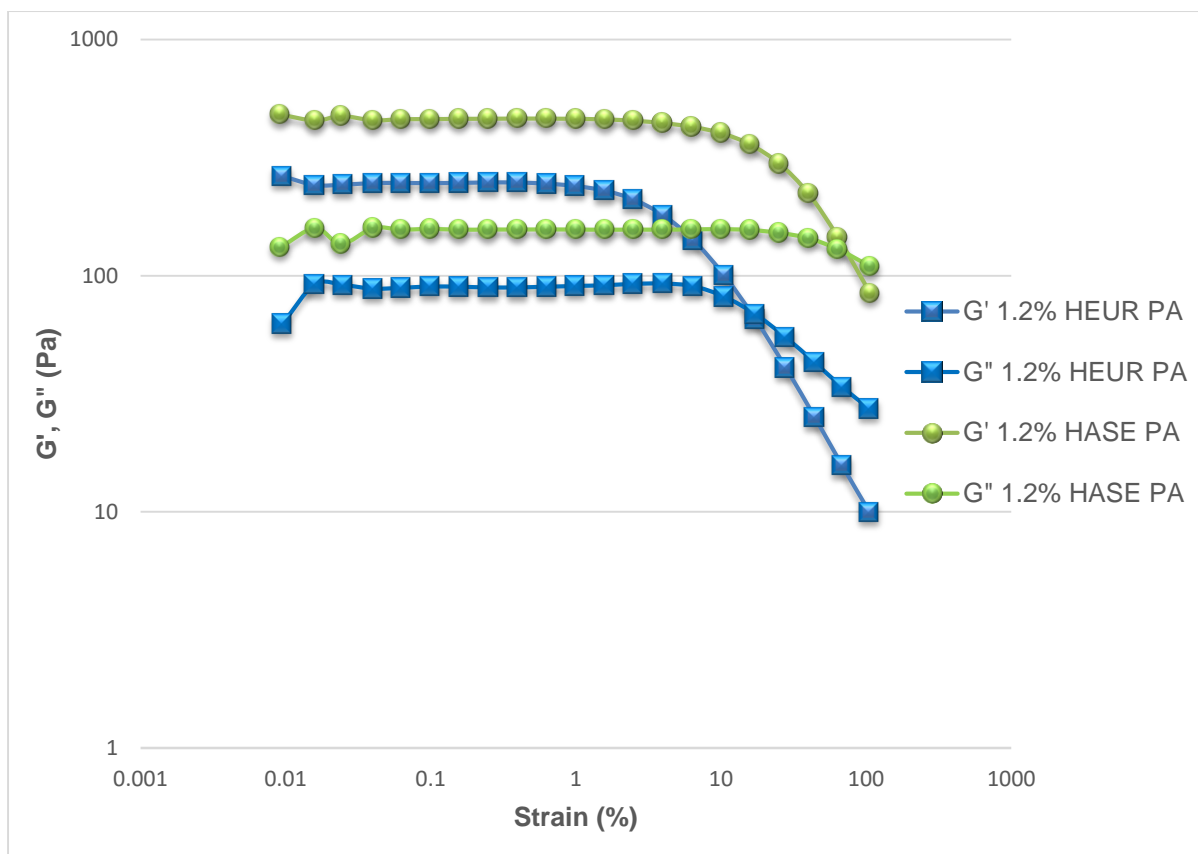


Figure 4.10: Amplitude sweep test results for paints containing 1.2 percent HEUR and HASE in presence of pure acrylic (PA) binder

The formulation thickened with HASE rheology modifiers has a larger linear viscoelastic range (LVER) and a higher storage modulus in the LVER. The LVER can be observed in Figure 4.14 and Figure 4.15, respectively, as the strain range in which the G' and G'' are almost constant with increasing strain (Osterhold, 2000). The highest storage moduli (G') and largest LVER were found to be in the water-based paint formulated with a 1.2 percent HASE, followed by the paint containing 0.8 percent HASE rheology modifier. For instance, at a 1 percent strain in the presence of PA binder, G' of paint with 1.2 percent HASE was found to be a 462.18 Pa, sample with 0.8 percent HASE recording a G' of 320 Pa.

The storage moduli of 0.8 percent HEUR and 1.2 percent HEUR at the 1 percent strain was determined to be 305.22 Pa and 239.96 Pa respectively. The higher storage modulus signifies a stronger internal structure because its elastic behaviour is dominant and improves the storage stability of paint (Haramagatti et al., 2018). The larger LVER indicated that greater energy is required in order to break the internal structure of this sample of water based paint (Haramagatti et al., 2018).

This implies that a HASE rheology modifier imparts more elastic behaviour and better in-can stability to water-based paints than the HEUR rheology modifiers. This finding agrees with

Hussain and Nasr (2010), who found that HASE thickener does not only improve the viscosity of water based paint but also enhances stability due to the electrostatic repulsion between carboxylate groups present in the binder particles (Hussain & Nasr, 2010). Although the strong structure imparted by a HASE rheology modifier has a positive influence on the storage stability, it can negatively affect the ease of application, flow, and levelling after application.

At a concentration level of 0.8 percent in the presence of a PA binder, as shown in Figure 4.14, G' of HEUR and HASE; rheology modifiers are comparable from a 0.01 percent to a 1 percent strain. However, the sample of paint with 0.8 percent HASE has a larger LVER. This infers that although these two samples have the same degree of elasticity at some stage, the sample of paint containing 0.8 percent HEUR will not require a large amount of energy to destroy its internal structure.

It can be deduced that paint thickened using a HEUR rheology modifier is more likely to be unstable during storage (Reuvers, 1999), but it will possess better application properties and provide good levelling after application. The storage modulus in the LVER was found to be increasing as the concentration of the HEUR rheology modifier increased. For instance, G' at a 0.1 percent strain of the paint sample with 0.8 percent HEUR and 1.2 percent HEUR was found to be 111.47 Pa and 247 Pa, respectively. In the case of a HASE rheology modifier G' increased as the thickener concentration increased.

The crossover point between G' and G'' can be used to predict the ease of application, levelling and flow upon application (Auschra et al., 2015). The results in Figure 4.14 and Figure 4.15 show that paint thickened with a HEUR rheology modifier have a crossover point at lower strain than in paint with a HASE rheology modifier. For instance, paint made with a PA binder with 0.8 percent and 1.2 percent HEUR, had their $G'-G''$ crossover at 11.7 percent and 17.2 percent strain, respectively.

The crossover of G' and G'' of samples with 0.8 % HASE and 1.2 percent HASE was observed to be at 64.3 percent and 64.1 percent, strain respectively. This suggests that paints with HEUR rheology modifiers are expected to have adequate ease of application and good levelling after their application. Auschra et al. (2015) also found that HEUR thickeners produce better flow and levelling upon application than HASE. Furthermore, these observations agreed with findings from a flow curve test which established that paints with HEUR thickener are expected to produce adequate application properties.

Figure 4.16 and Figure 4.17 below illustrate the dynamic amplitude sweep results of paint formulation thickened with HASE and HEUR rheology modifiers, in the presence of styrene acrylic (SA) binders.

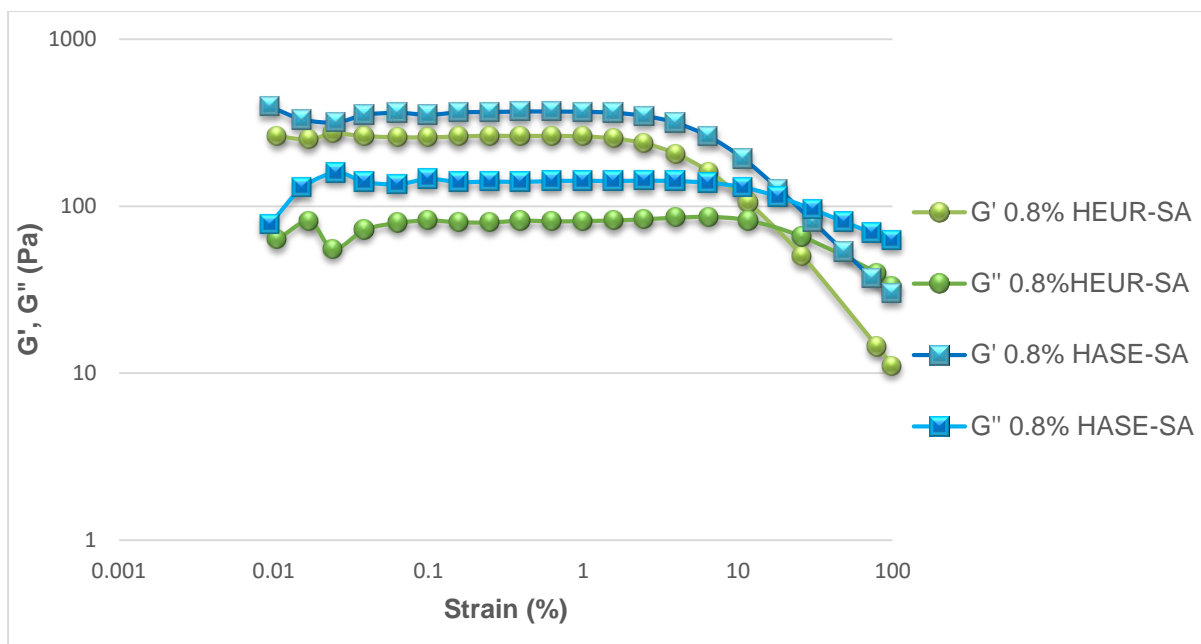


Figure 4.11: Amplitude sweep test results for paints containing 0.8 percent HEUR and HASE in presence of SA binder.

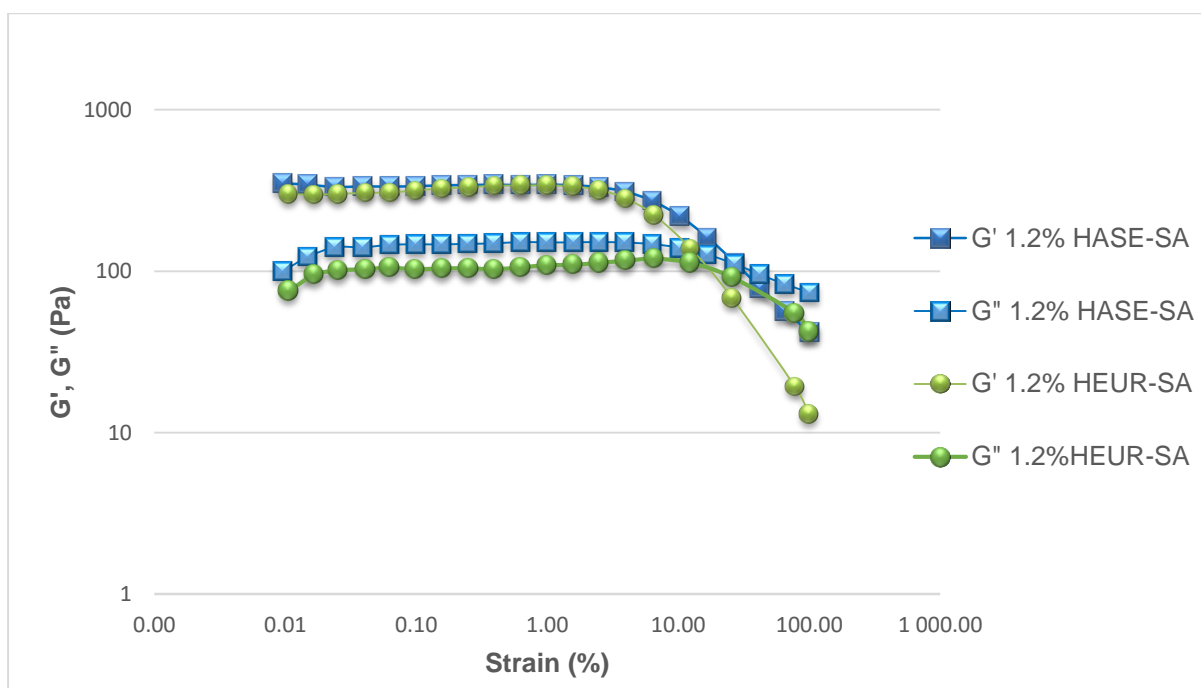


Figure 4.12: Amplitude sweep test results for paints containing 1.2 percent HEUR and HASE in presence of SA binder.

In the presence of styrene acrylic (SA) binders, just like for the pure acrylic (PA) binder, the elastic behaviour is dominant in the LVER. The highest storage modulus in the LVER was found to be in the sample containing 1.2 percent HASE, followed by 0.8 percent HASE rheology modifiers. The storage moduli of 1.2 percent HASE and 0.8 percent HASE at a 1 percent strain was determined to show 376.5 Pa and 366.9 Pa, respectively. This implies that irrespective of the type of binder used, HASE rheology modifiers impart a more elastic

behaviour to water-based paints than HEUR thickener. The advantage of high elasticity in the LVER is that the sample of paint containing HASE rheology modifiers will possess good storage properties and will be likely to resist sagging (Gina Paroline, 2016). However, high elasticity (i.e., stiffness and strong internal structure) may negatively affect application properties such as ease of application and levelling of the layer of paint, after application.

Analysing the crossover points between G'' and G' of paint made with an SA binder. It can be observed that paints with HEUR rheology modifiers have their crossover points at a lower strain level than HASE based paints. For instance, the crossover point of 0.8 percent HEUR and 1.2 percent HEUR was observed to be at the 26.2 percent and 25.2 percent strains, respectively. The storage and loss moduli crossover points of 0.8 percent HASE and 1.2 percent HASE in the presence of SA, were observed to be at 30 percent and 27 percent, respectively. This suggested that paints containing HEUR are expected to have better ease of application and flow during application (Auschra et al., 2015). To illustrate the effect of each type of thickener on the viscoelasticity of paint, the dynamic amplitude sweep test data of paint samples at a 0.8 percent concentration of both HEUR and HASE, in the presence of PA and SA binders will be analysed. Figure 4.18 below shows the Dynamic Amplitude Sweep test of paints with concentration 0.8 percent of both associative thickeners, in the presence of styrene and pure acrylic binders.

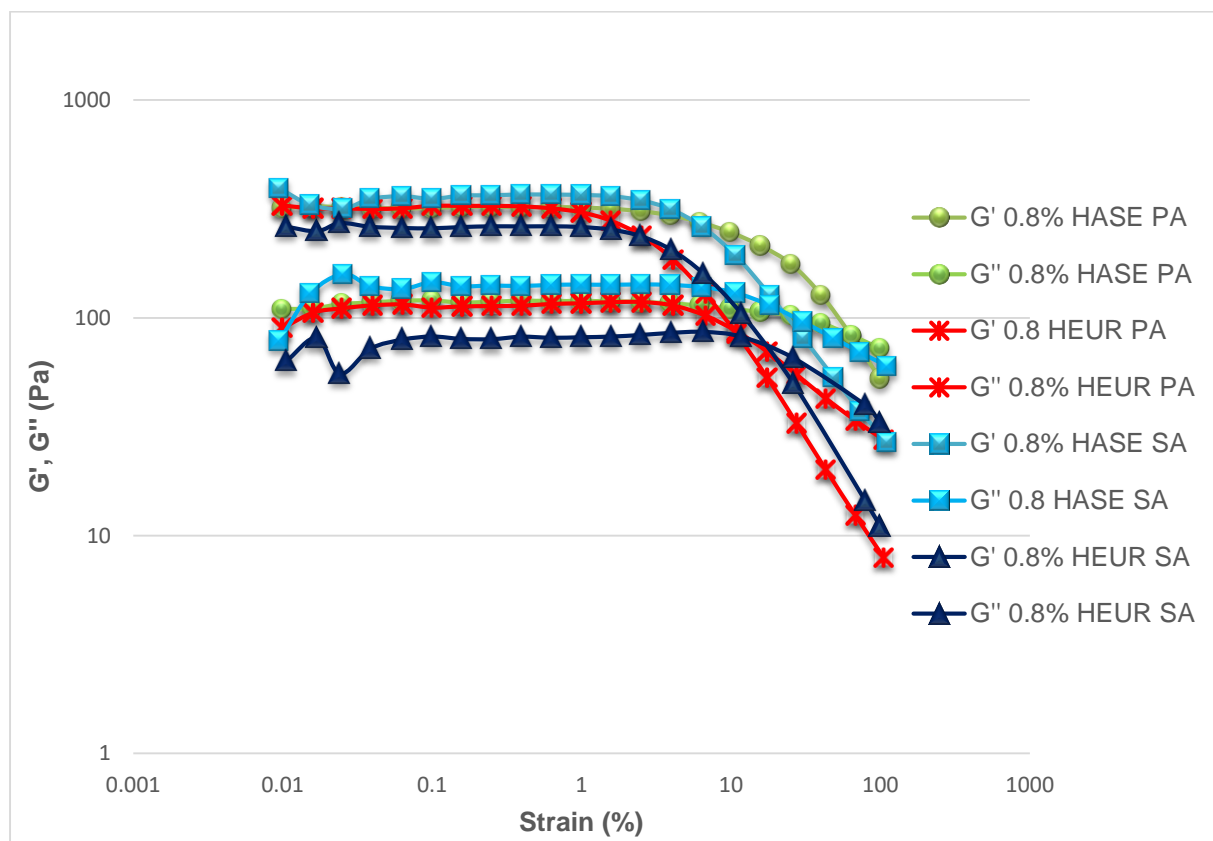


Figure 4.13: Performance of HEUR and HASE at concentration 0.8 percent

It can be seen from the results that at a 0.8 percent thickener concentration, irrespective of the type of binder, all samples of paints possess a dominant elastic character in the LVER, and samples thickened by HASE have a longer LVER than the paint samples thickened by HEUR thickened samples. The storage modulus of samples containing 0.8 percent HEUR in the presence of pure acrylic (PA) binders is higher than the G' of samples thickened by HEUR in the presence of a styrene acrylic (SA) binder. However, G' of samples containing 0.8% HASE rheology modifier in the presence of a PA binder is lower than the G' of samples thickened by HASE, in the presence of an SA binder. The reason for the lower elastic behaviours of paint samples containing HASE thickener, in the presence of a styrene binder could be linked to the higher hydrophobicity of styrene binders which hinders the swelling carboxyl groups contained in the HASE rheology modifier (Šňupárek & Quadrat, 2006).

To show the contribution of higher thickener concentration to the viscoelasticity of paint, data from the dynamic amplitude test at a 1.2 percent concentration of HASE and HEUR, in the presence of PA and SA binders, will be examined.

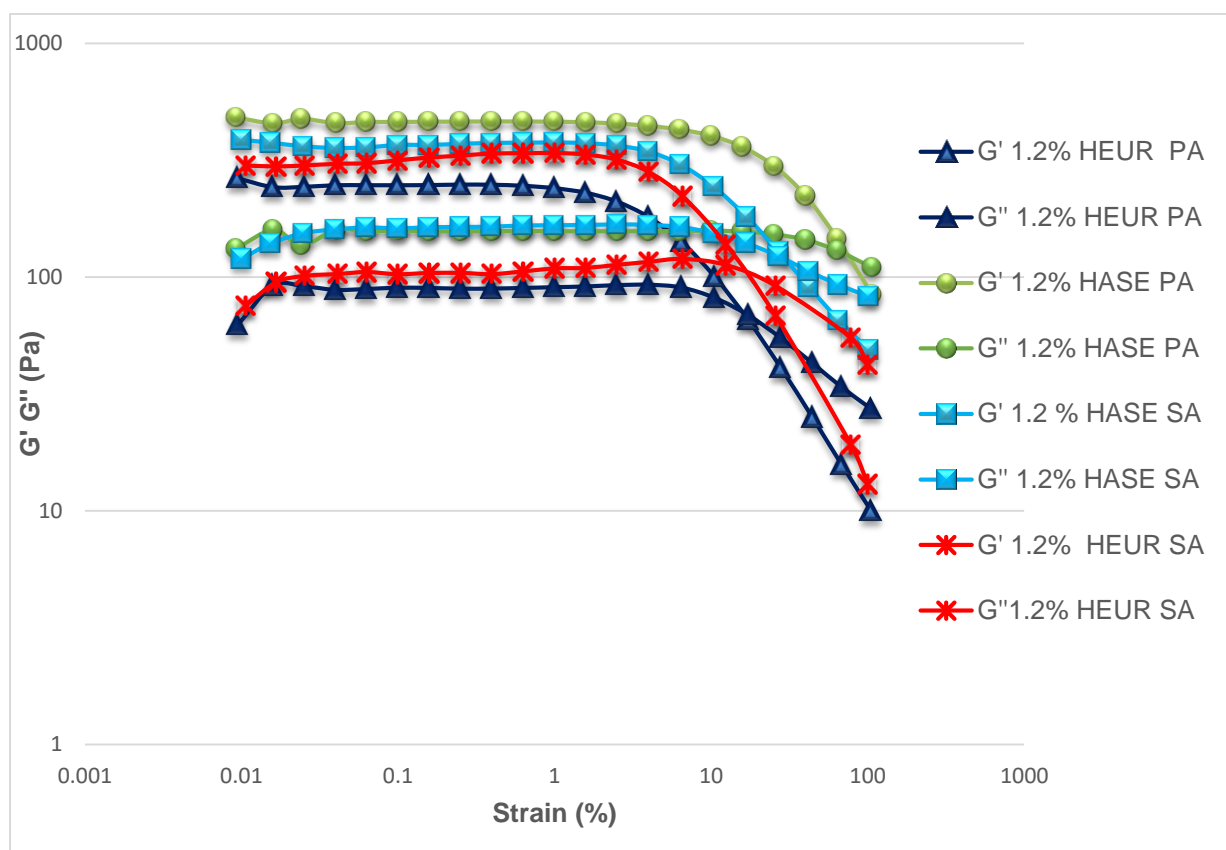


Figure 4.14: Performance of HEUR and HASE at concentration at 1.2 wt. percent

The results in Figure 4.19 above present the amplitude sweep results of paint samples containing 1.2 percent both HASE and HEUR. The highest storage modulus in the LVER was found in samples of paint thickened by HASE rheology modifiers in the presence of PA binders

which have an approximately constant G' of 462 Pa in the LVER, followed by 1.2 percent HASE in the presence of SA binder with a G' of 376 Pa in the LVER at 1 percent strain. The storage modulus of paint samples containing 1.2 percent HEUR, in the presence of styrene binders was found to be higher than the sample containing pure acrylic binder. For instance, at a 1 percent strain G' of paint samples thickened with 1.2 percent the HEUR was found to be 239.96 Pa for a PA binder and 339 Pa for an SA binder. For both types of binder, HASE rheology modifiers have larger LVER than HEUR. These findings show that the type of binder can affect the LVER and has a significant influence on the storage and loss moduli of water-based paint. The results of the yield stress from amplitude sweep data are summarised in Table 4.14 below.

Table 4.14: Yield stress results from amplitude sweep at constant temperature (25°C) and frequency (1Hz).

<i>Thickener type and concentrations</i>	<i>Yield stress (Pa)</i>	
	<i>Pure acrylic binder</i>	<i>Styrene binder</i>
0%	6	4
0.8% HEUR	9	11
0.8% HASE	38	19
1.2% HEUR	11	14
1.2% HASE	62	30

For pure and styrene acrylic binders, the results in Table 4.14 show that paint samples containing HASE rheology modifiers have higher yield stress values than samples thickened with HEUR. The reason for such a finding can be ascribed to the larger LVER of paint samples containing HASE rheology modifiers. The highest yield stress was found to be in the paint sample thickened with 1.2 percent HASE, followed by a 0.8 percent HASE, with a 1.2 percent HEUR and a 0.8 percent HEUR. The paint samples without rheology modifiers were determined to have the lowest yield stress.

Based on these results, it can be observed that there is a direct correlation between the yield stress and the rheology modifier concentration. The finding is in agreement with Moolman (2003) who established that yield stress increases with increasing thickener concentration. Paint samples made of pure acrylic binder generated higher yield stress values than samples containing styrene at each thickener concentration. This can be ascribed to the fact that the thickening efficiency of association rheology modifiers is greatly influenced by their

interactions with binder particles. The yield stress values of HASE thickener in the presence of pure acrylic binders is nearly two times larger than the yield stress generated by this thickener, in the presence of styrene binder at each concentration.

The yield stress values produced by HEUR thickener in the presence of pure acrylic binder can be observed to be close to the yield stress value produced by this particular thickener in the presence of a styrene binder. These results confirm that the HASE rheology modifier has a higher thickening efficiency in the presence of a pure acrylic binder and that HEUR rheology modifier performance is not greatly affected by the type of binder used.

Comparing the yield stress results from the dynamic amplitude test and the yield stress data obtained from the rheological models in sections 4.3.2- 4.3.4, it can be observed that the yield stress results from the dynamic amplitude sweep test differing from the yield stress that occurs, when using the rheological models. The reason for this could be linked to the fact that the data from the rheological models was obtained from the flow curve test, which only describes the flow parameters of paint, while the yield stress from the dynamic amplitude test takes into consideration the viscous as well as the elastic behaviours of paint.

Although the yield stress values from a dynamic amplitude test are not identical to the yield stress obtained from the rheological models, there are a few similar trends. For instance, irrespective of the type of binder, paint samples with a 1.2 percent HASE have the highest yield stress, followed by paint samples with a 0.8 percent HASE. Furthermore, the lowest yield is observed to come from the paint samples without thickener.

4.5. Three Interval Thixotropy Test (3ITT)

As outlined in chapter three, the Three Interval Thixotropy Test (3ITT) measures rheological parameters under three different conditions. The first interval was performed in the oscillation mode at a frequency of 1Hz and a strain of 0.1 percent, for a period of 60 minutes. The second interval was conducted in the rotational mode at a shear rate of 1000 s^{-1} for a period of 120 minutes; and the third interval was conducted under the same conditions as the first interval, but for periods of 10 minutes. For this, the storage modulus (G') recovery was investigated, because for all experimental paint samples, G' is greater than the loss modulus (G'') in the third interval, implying that all the paint samples are predominantly elastic under the high shear load (Moolman, 2003).

Figure 4.20 and Figure 4.21 below illustrates the results from the 3TT of paint made with pure acrylic binder. Table 4.15 below shows the percentage recoveries of paint samples under the high shear condition.

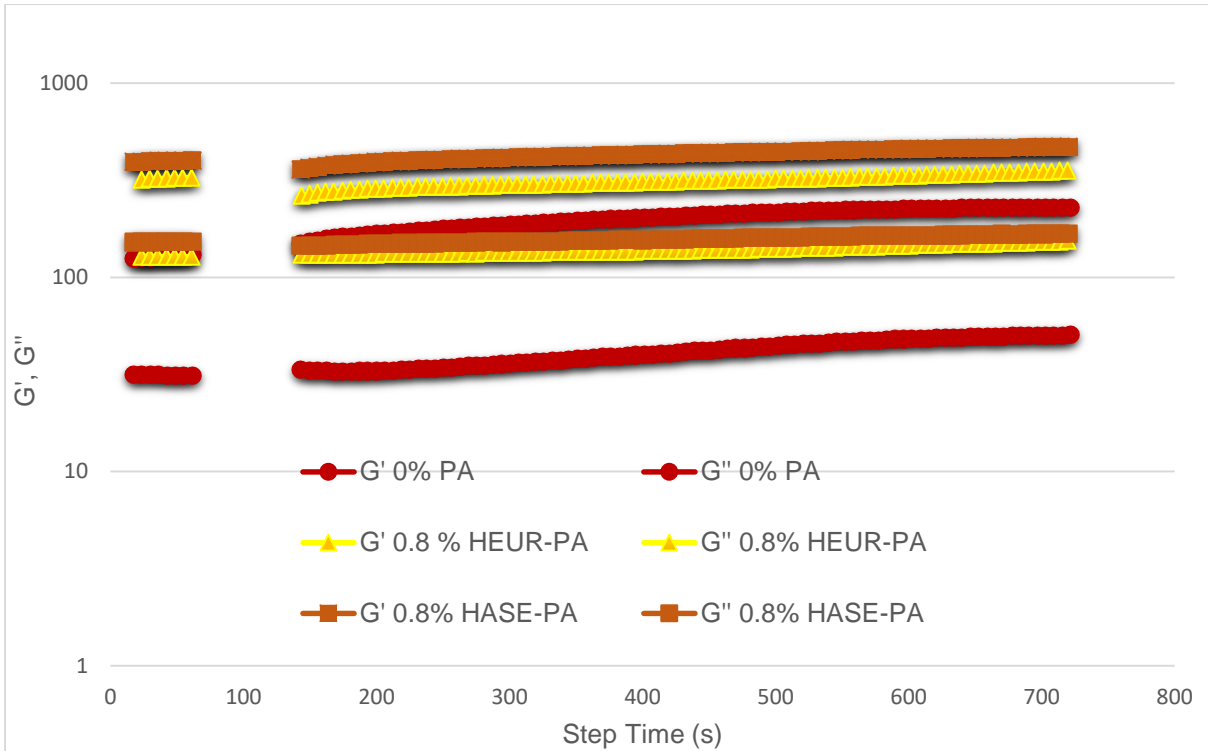


Figure 4.15: 3ITT results for paint samples containing pure acrylic binder (0 percent and 0.8 percent thickener concentration).

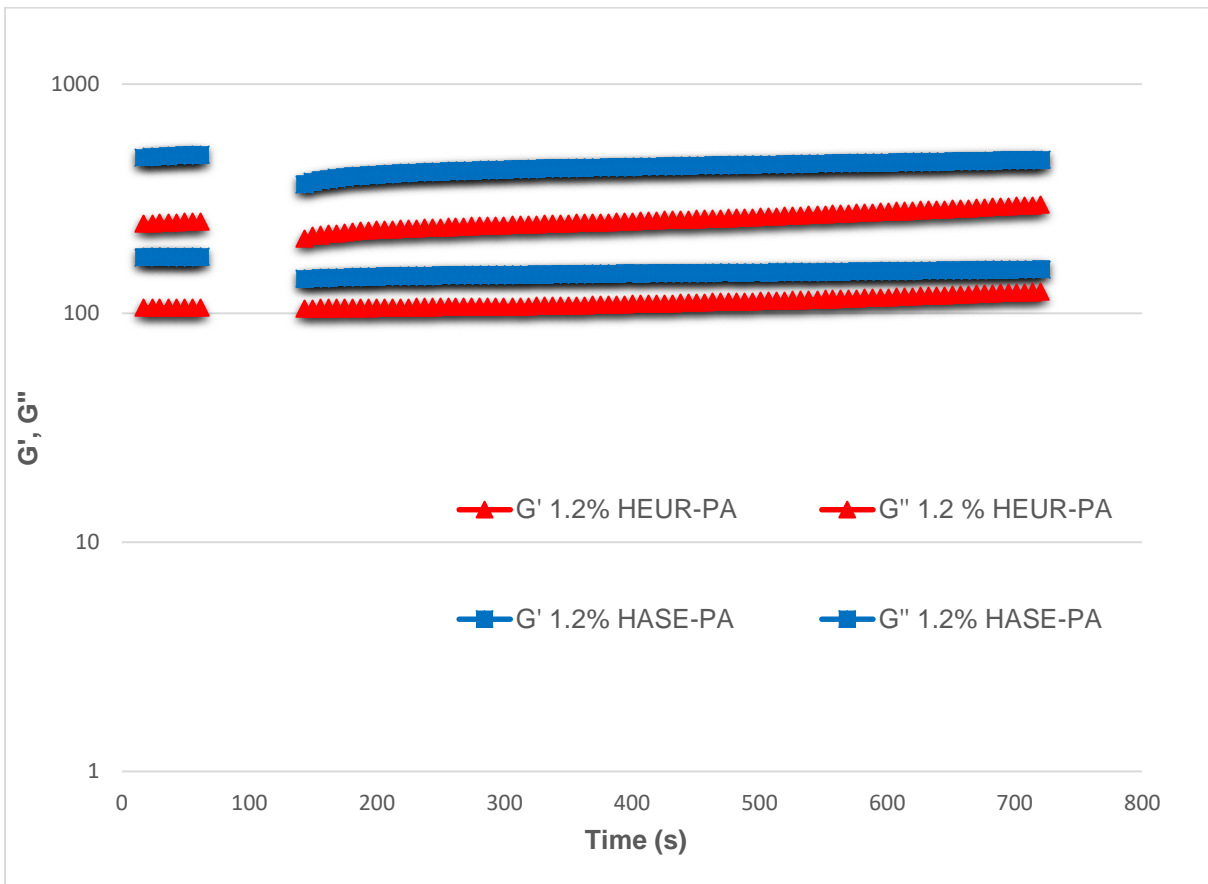


Figure 4.16: 3ITT results for paint samples containing pure acrylic binder (1.2 percent thickener concentration).

Table 4.15: Storage modulus percentage recovery for pure acrylic based samples
Storage modulus recovery (%)

Time (s)	0%	0.8% HEUR	0.8% HASE	1.2% HEUR	1.2% HASE
1	114	80.5	90	85	75
5	122	85	95	89	79
10	126	87	98	92	82
20	136	90	102	95	85
60	166	98	111	105	91
100	174	107	117	116	94.4

For all the paints containing pure acrylic binder at different thickener concentrations, it can be observed that the storage modulus is greater than the loss modulus before and after the high shear.

Table 4.15 shows that the sample with a 0% thickener concentration, which has the lowest viscosity has the highest and the fastest structure recovery after the high shear rate load. The storage modulus of the paint with 0% thickener was 130.6 Pa at the end the first interval, and 149.4 Pa after the first second the first interval. Bhavsar and Shreepathi (2016) similarly found that the viscosity recovery of water based paint samples with low viscosity was higher and faster than the paint samples with higher viscosity. This implies that after application of this sample of paint, the film will not experience sagging but will have very poor levelling, resulting in brush marks.

Table 4.15 shows that the slowest structure recovery was determined as being with the sample containing 1.2 percent HASE rheology modifier which has a 75 percent recovery one second after the high shear and a 94 percent recovery rate a hundred seconds after the high shear rate. After the 1.2 percent HASE sample followed the paint sample with a 0.8 percent HEUR with 81 percent and 98 percent structure recovery at the first and at the 60th second in the third interval, respectively, as shown in Table 4.15.

Bhavsar and Shreepathi (2016) reported that slower recovery could be linked to the viscosity of paint during the high shear period. It was determined that high viscosity at the higher shear rate does not only lead to a larger film build, but also to slower structure regeneration which could lead to better flow and levelling after paint application (Bhavsar & Shreepathi, 2016). The data obtained correlated correctly with the findings of Bhavsar and Shreepathi (2016) as the sample with 1.2 percent HASE had the highest viscosity in the high shear at a high shear rate condition and the slowest structure recovery. Furthermore, paint samples with of 0.8

percent and 1.2 percent HEUR have comparable viscosities at high shear rate conditions and produced close structure recoveries. Another advantage of a slower structure recovery is a longer open time, thus allowing the painter to correct the applied film of paint, using a brush or roller (Overbeek et al., 2003).

The results obtained in table 4.16 below suggest that in the presence of a pure acrylic binder, all the paint samples except the unthicken i.e., 0 percent sample will experience good flow and levelling after their application as their G' recovery is below 100 percent between the 20 and 60 minutes after the high shear condition i.e., the structure of these paint samples after shear load will take time to reach their initial structure. This infers that the sample of paint containing HASE thickener will yield more film thickness (Franck, 2004). Franck (2004) reported that film thickness is greatly affected by the elasticity of paint after its application.

Figure 4.22 and Figure 4.23 illustrate the results from the 3ITT of paint made of styrene acrylic binder. Table 4.16 below shows the percentage recoveries of styrene acrylic binder-based paint samples after the high shear condition.

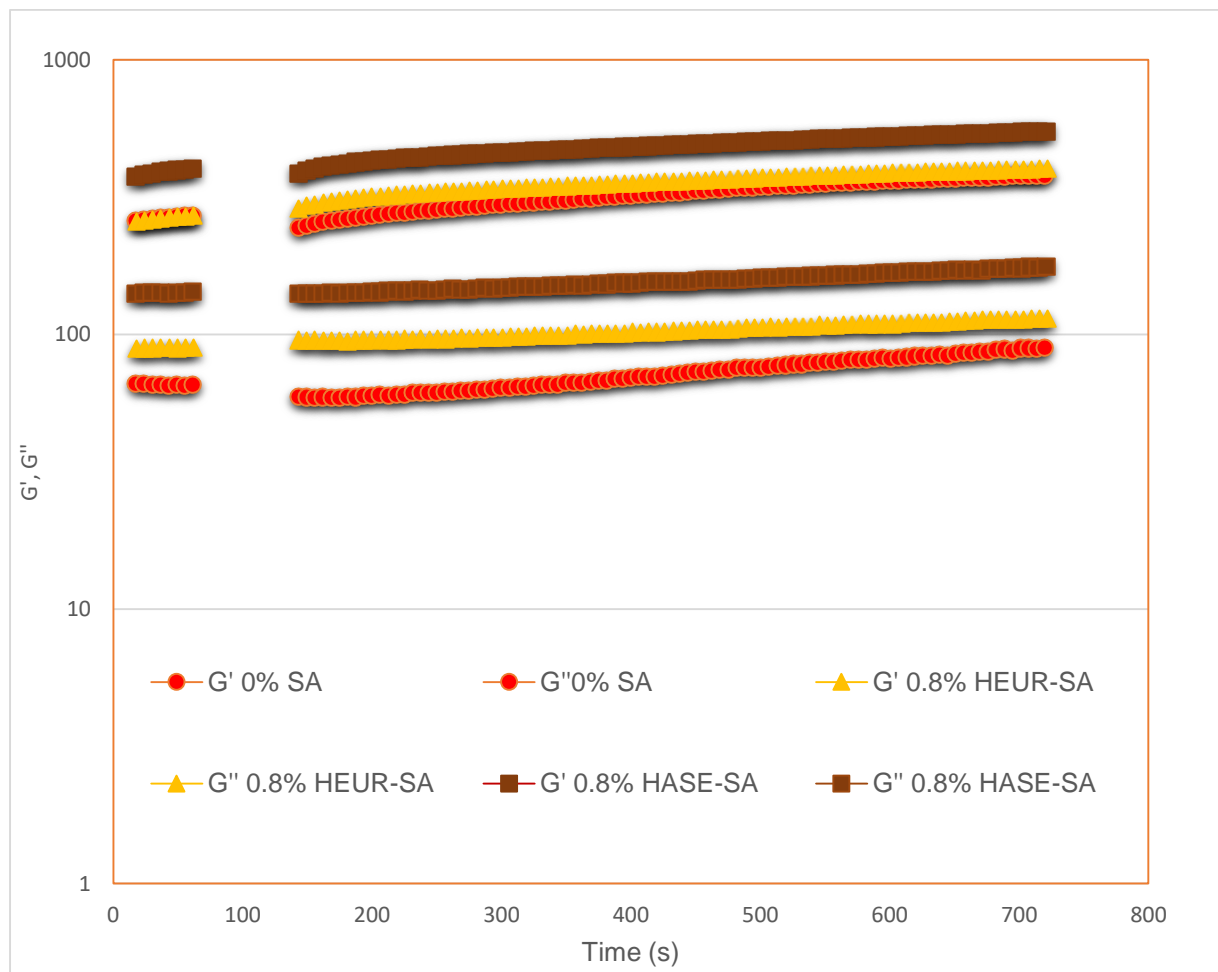


Figure 4.17: 3ITT results for paint sample containing styrene acrylic binder (0 percent and 0.8 percent thickener concentration)

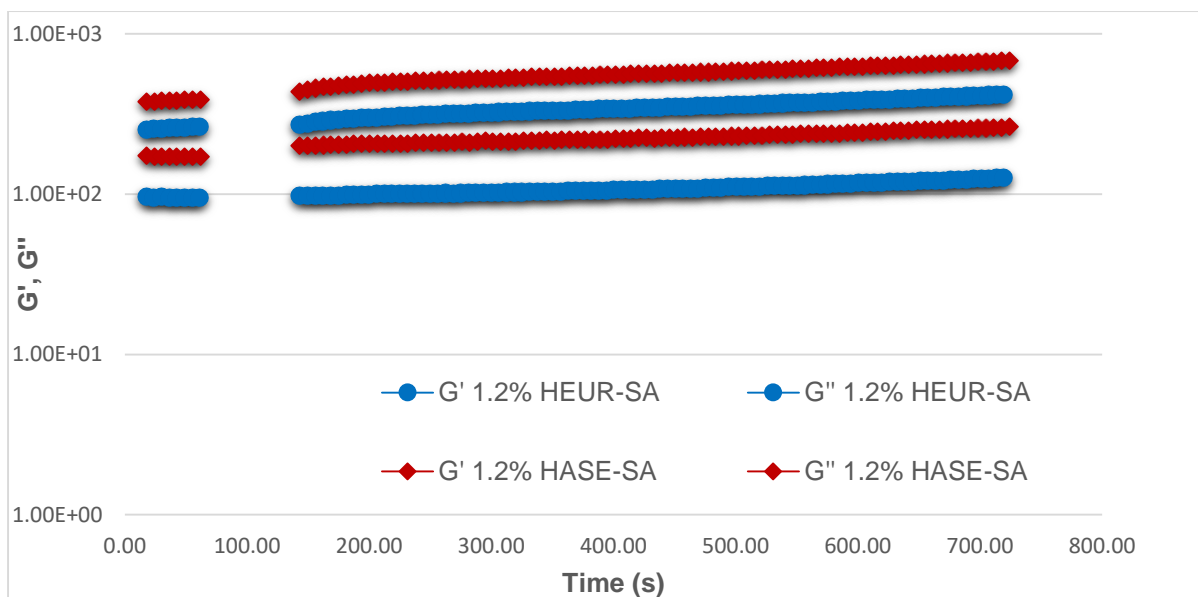


Figure 4.18: 3ITT results for paint samples containing styrene acrylic binder (1.2 percent thickener concentration).

Table 4.16: Storage modulus percentage recovery for styrene acrylic-based samples

<i>Time (s)</i>	<i>Storage modulus recovery (%)</i>				
	0%	0.8% HEUR	0.8% HASE	1.2% HEUR	1.2% HASE
1	92	106	96	102	112
5	98	113	103	109	121
10	103	117	107	114	127
20	111	122	112	120	133
60	136	137	126	137	152
100	146	147	135	155	171

Comparing the paint structure results of paint made with pure acrylic and styrene as shown in Table 4.15 and Table 4.16, respectively; it is apparent that a sample of paint made with a styrene binder was found to yield faster storage modulus recovery after high shear load than pure acrylic binder. This finding could be ascribed to the fact that PA and SA binders differ not only chemically but in particle size as well (Quadrat et al., 2005).

For instance, 5 seconds after the high shear load, all paint samples made of styrene acrylic, irrespective of the type of thickener used, were found to have structure recovery beyond their initial structure (i.e., more than a 100 percent of G' recovery), as shown in Table 4.16. The fast recovery of paint is beneficial towards sag resistance but is not good for levelling because paint will stop flowing after application, leading to brush marks after the layer of paint has

dried. This agrees with Bhavsar and Shreepathi (2016) who reported that binder composition can affect the thickening of water based paints and hence their overall rheology and application properties.

According to Moolman (2003), the fast rate of structure recovery of the paint samples made with styrene acrylic binder indicate that these samples will have a greater film thickness when applied. Moolman (2003) established that there is a relationship between the paint film thickness and the rate of its storage modulus recovery. This suggests that paint samples made of styrene acrylic will yield a larger film thickness during their application.

4.6. Dynamic Frequency sweep

As explained in chapter three, the dynamic frequency test measures the change of G' and G'' with increasing frequency, ranging from 0.01 to 100 rad/s. In this study, this test was conducted at a constant strain of 0.1% and a constant temperature of 25°C.

The dynamic frequency test results of paint made with pure acrylic binder are shown in Figure 4.24 and Figure 4.25 below.

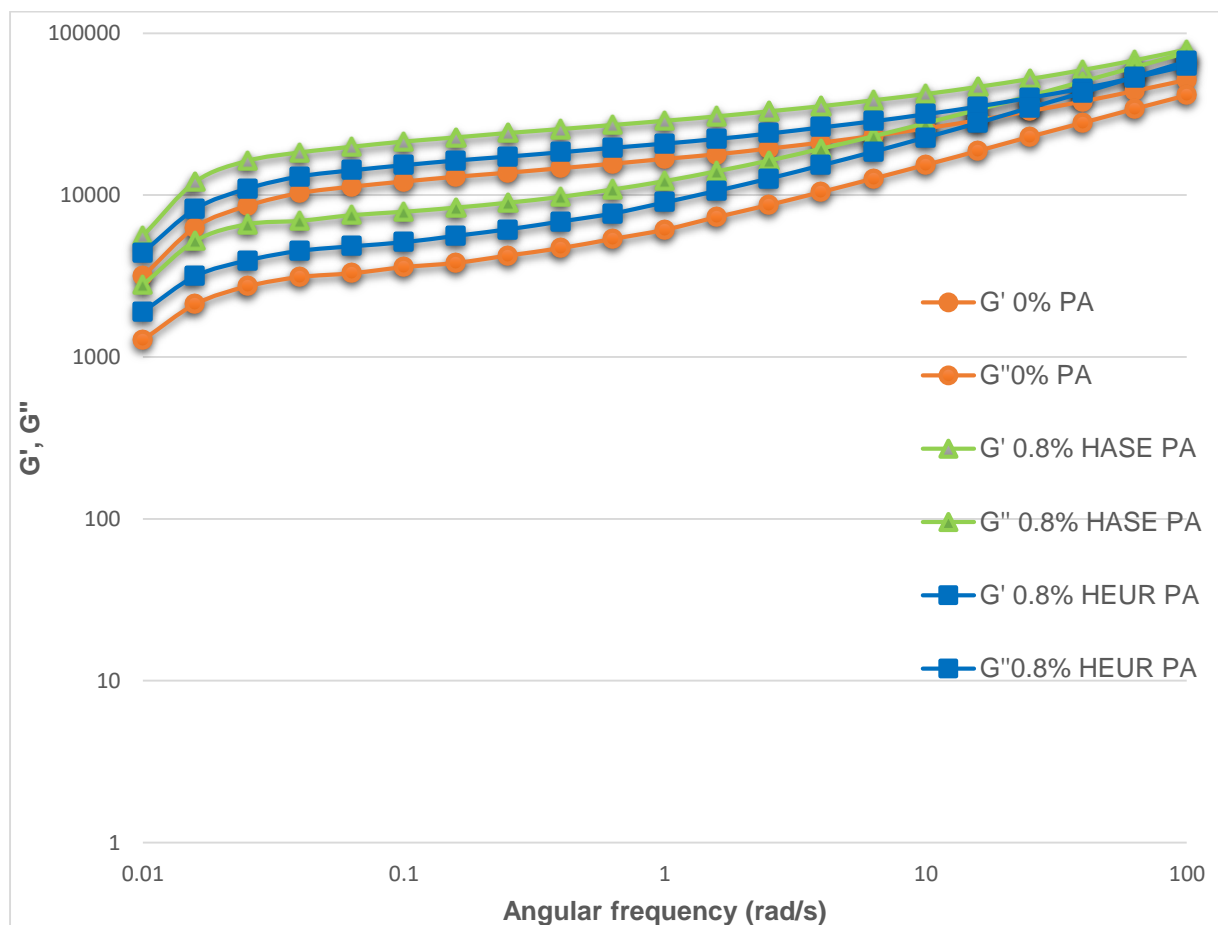


Figure 4.19: Frequency sweep results of pure acrylic based paint samples (0 percent and 0.8 percent thickener concentration)

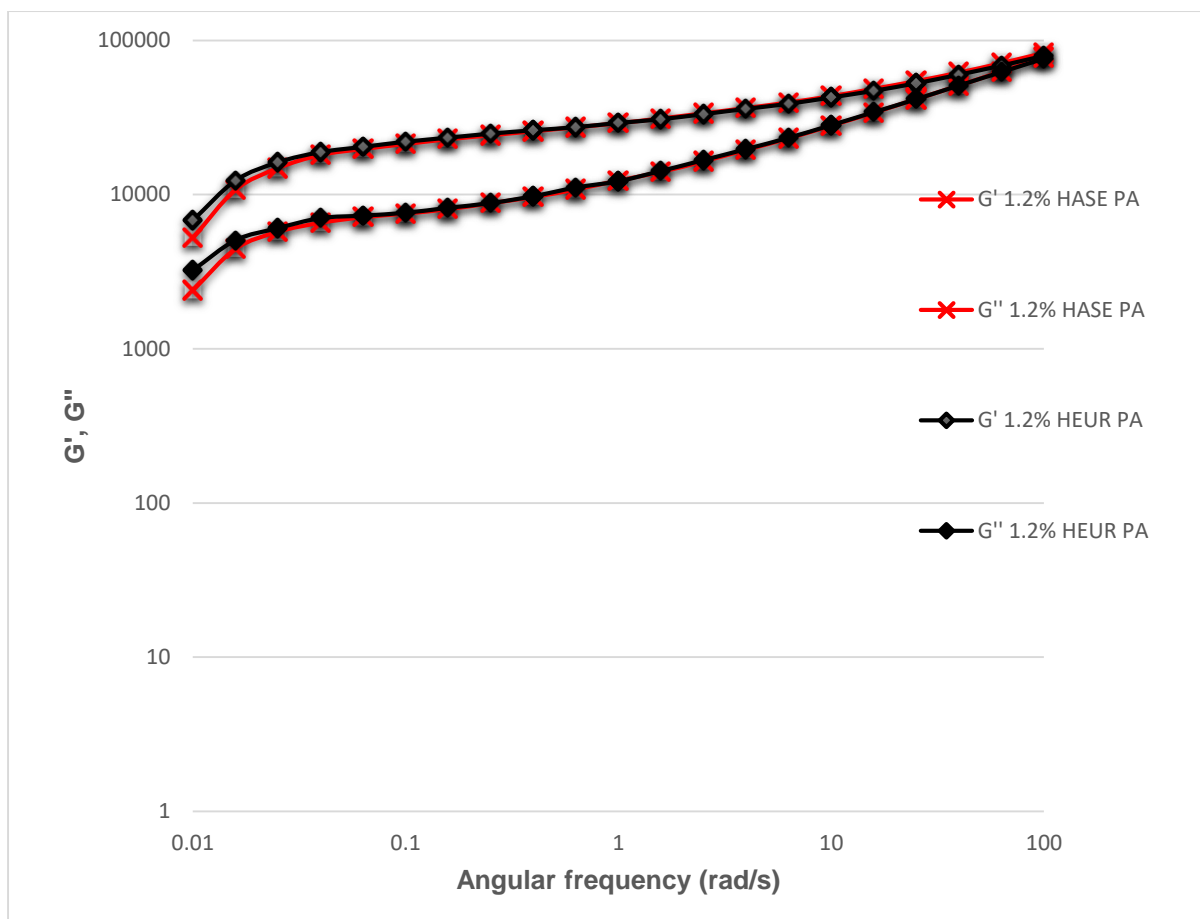


Figure 4.20: Frequency sweep results of pure acrylic based paint samples (1.2 percent thickener concentration)

Figure 4.24 represents the results of frequency sweep at a 0.1 percent strain of paint samples containing pure acrylic and thickened with HASE and HEUR at 0 percent, and 0.8 percent. Figure 4.25 represents the frequency sweep results of PA binder-based paints at 1.2 percent concentrations. In the low and medium frequency range (i.e., from 0.01 to 0.1 rad/s) the storage modulus is observed to be higher than the loss modulus for all the paint samples, irrespective of thickener type and concentration. This indicates that in the medium frequency range, all the sample are dominantly elastic i.e., solid like. However, in the high frequency region (from 80 rad/s to 100 rad/s) G'' increased almost tenfold. For example, the G'' of the 0.8% HASE at a frequency of 0.1 rad/s was determined to be 7.9×10^3 Pa and at a frequency of 100 rad/s G'' was found to be 7.55×10^4 Pa. Similarly, a G'' of 0.8 percent HEUR was found to be 5.12×10^3 Pa and 6.70×10^4 Pa at 0.1 and 100 rad/s frequencies, respectively. This indicates that at high frequencies, the viscous behaviour was dominant in all paint samples. The complex viscosity which is the ratio of G'' to the angular frequency will significantly decrease at high frequencies. These findings are in agreement with the results obtained for the viscosity curve tests, where it was determined that all paint samples were shear thinning (Kästner, 2001; Overbeek et al., 2003). The fact that the viscosity has dropped at high

frequencies is beneficial for the ease of application of paints using a brush or a roller (Mezger, 2014). Figure 4.26 and Figure 4.27 below show the results of dynamic frequency tests of paint samples made with a styrene acrylic binder.

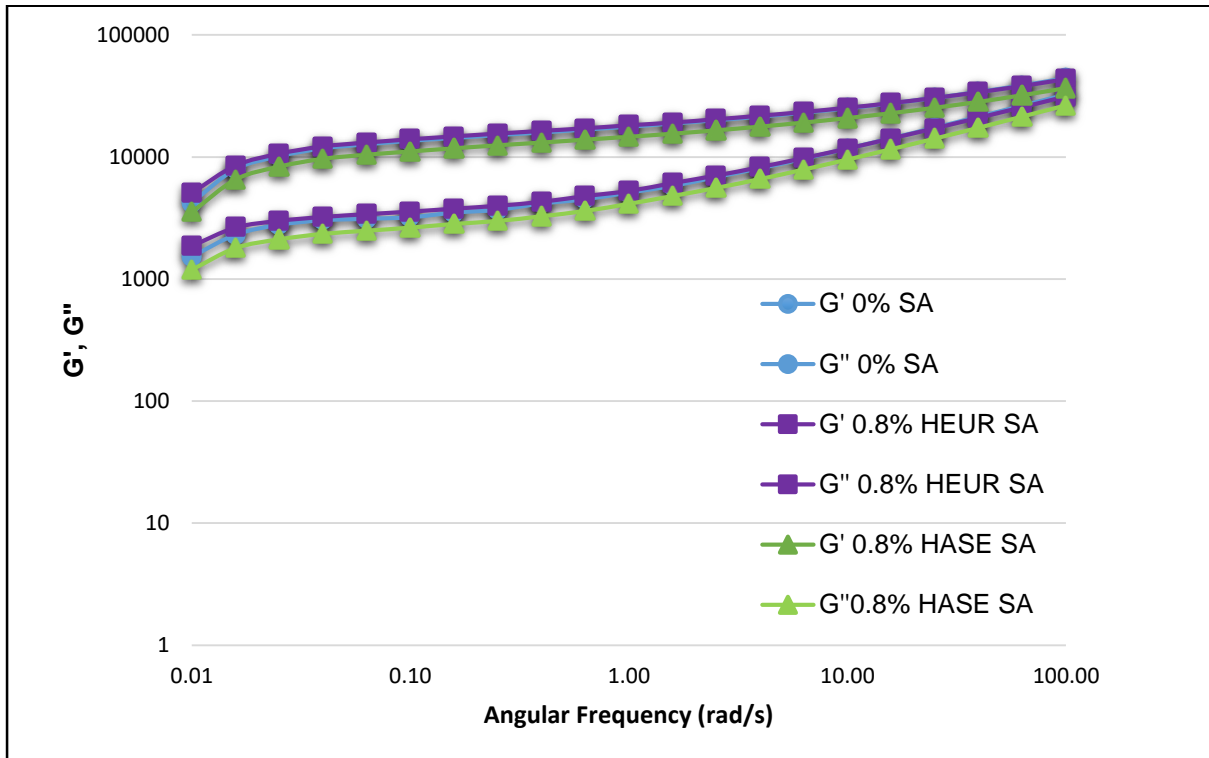


Figure 4.21: Frequency sweep results of styrene acrylic-based paint samples (0 percent and 0.8 percent thickener concentrations)

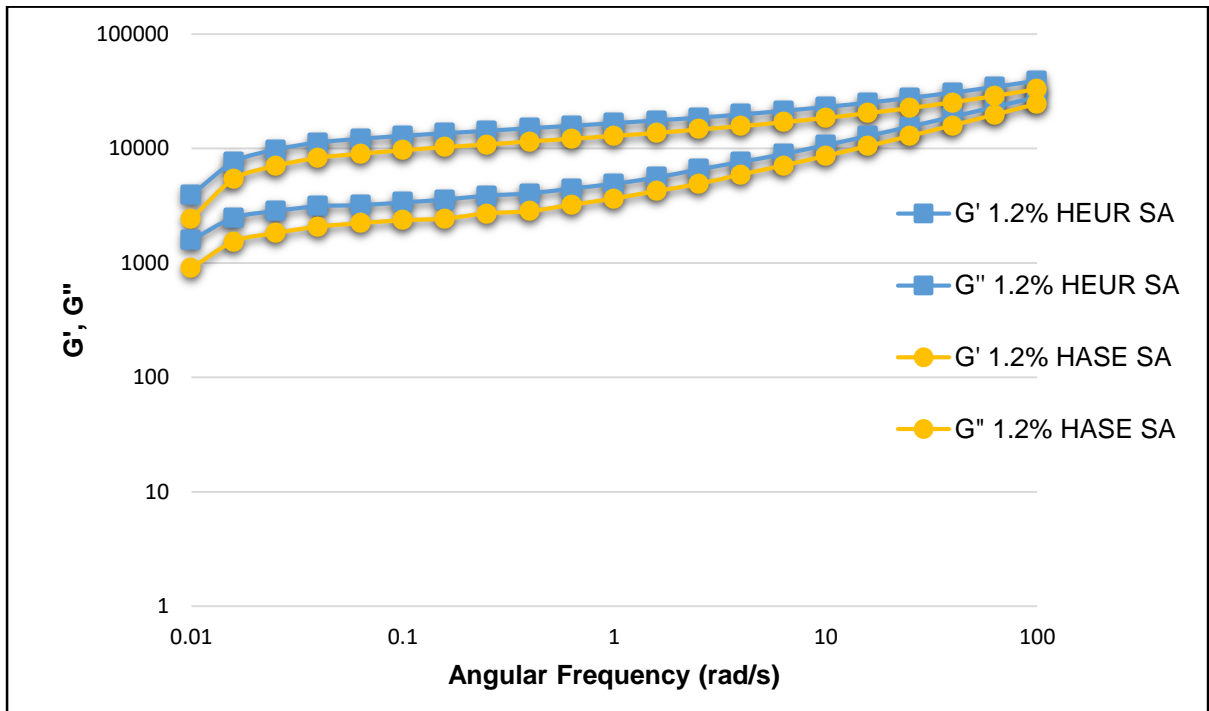


Figure 4.22: Frequency sweep results of styrene acrylic-based paint samples (1.2 percent thickener concentrations)

Figure 4.26 and Figure 4.27 show the results of frequency sweeps at a 0.1 percent strain of paint samples containing styrene acrylic binder and thickened with HASE and HEUR at concentrations varying from 0 percent to 1.2 percent. For the samples based on pure acrylic binder, the loss modulus was found to be increasing at a faster rate than the storage modulus with increasing angular frequency. At higher frequencies (from 80 to 100 rad/s), the storage and loss modulus tend to be comparable, as shown in Figure 4.27 and Figure 4.28. This signifies that at higher frequencies all samples are predominantly viscous (Kästner, 2001). The paint sample without thickener was found to have the highest loss modulus throughout the angular frequency range; followed by the samples 0.8 percent and 1.2 percent HEUR thickener which have very comparable G'' . For example, at an angular frequency of 100 rad/s, G'' of paint of 0 percent, 0.8 percent HEUR and 1.2 percent HEUR was determined to be 3.25×10^4 Pa, 3.15×10^4 Pa and 2.82×10^4 Pa, respectively. These findings correctly correlate with the viscosity curve results in the presence of styrene binders as shown in Figure 4.8 and Figure 4.9. The sample without thickener had low viscosity values at a given shear rate which corresponds to higher G'' i.e., less elastic. The lowest G'' was found to occur with samples thickened with a HASE rheology modifier. This indicates that HASE imparts more elastic behaviour to paint than HEUR rheology modifiers. These findings confirm the results observed in the flow curve and amplitude sweep tests. It was found in the flow curve test that HASE leads to higher paint viscosities than HEUR; and it was established in the amplitude sweep that most paints containing HASE thickener have a larger LVER. The storage and loss moduli of 0.8 percent HASE has a larger G'' than 1.2 percent HASE, at any given frequency. For instance, at low frequency of 0.1 rad/s G'' of 0.8 percent HASE and 1.2 percent HASE were determined to be 2.64×10^3 Pa and 2.34×10^3 Pa, respectively. At a higher frequency of 100 rad/s, G'' of 0.8 percent HASE and 1.2 percent HASE was determined to be 2.64×10^4 Pa and 2.45×10^4 Pa, respectively.

These findings correctly correlate with the viscosity curve results in the presence of a styrene binder as shown in Figure 4.9. The samples without thickener had low viscosity values at a given shear rate, which corresponds to a higher G'' i.e., it is less elastic. Samples with 0.8 percent and 1.2 percent HEUR were found to have very comparable viscosities at a given shear rate. Similarly, in the frequency sweep their G'' was found to be comparable at a given angular frequency. For instance, at frequency 0.1 rad/s, G'' of 0.8 percent HEUR and 1.2 percent HEUR was found to be 3.57×10^3 Pa and 3.37×10^3 Pa, respectively. At a frequency of 100 rad/s G'' of 0.8 percent HEUR and 1.2 percent HEUR was determined to be 3.13×10^4 Pa and 2.82×10^4 Pa respectively. The sample with 1.2 percent HASE was found to have the highest viscosity throughout the viscosity profile, which corresponds to the lowest loss moduli, which, in turn, confirms that samples of with a HASE rheology modifier are predominantly

elastic in the presence of pure acrylic, as well as a styrene acrylic binder. On linking the results observed in Figures 4.22 - 4.27 to the paint performance, it can be concluded that all the experimental samples are expected to be stable on storage as the elastic behaviour is dominant in the low angular frequency region. For styrene acrylic as well as pure acrylic binder, samples containing HASE rheology modifiers were found to be more elastic than the ones containing HEUR rheology modifiers. This implies that samples with HEUR rheology modifiers will have improved ease of application i.e., the paint applicator will not require great force while applying these paints with brush or roller and excellent levelling characteristics after application.

4.7. Optical properties

In this section, the results of thickener type and concentration on some paint optical properties are presented. As this project deals with decorative water-based paint, it is important to analyse the influence of rheology on some aesthetic properties of paint. Furthermore, considerable research work has been done on the effect of pigment and PVC on the optical properties of paint, but the current literature hardly addresses the contribution of thickeners in the presence of different type binders on paint optical properties. Gloss and opacity or hiding power are the two optical properties that were investigated in this section. These properties were measured at constant film thickness of 200µm.

4.7.1. Effect of thickener type and concentration on gloss

Figure 4.28 below shows the effect of thickener type and concentration on the gloss of paint made of pure acrylic binder.

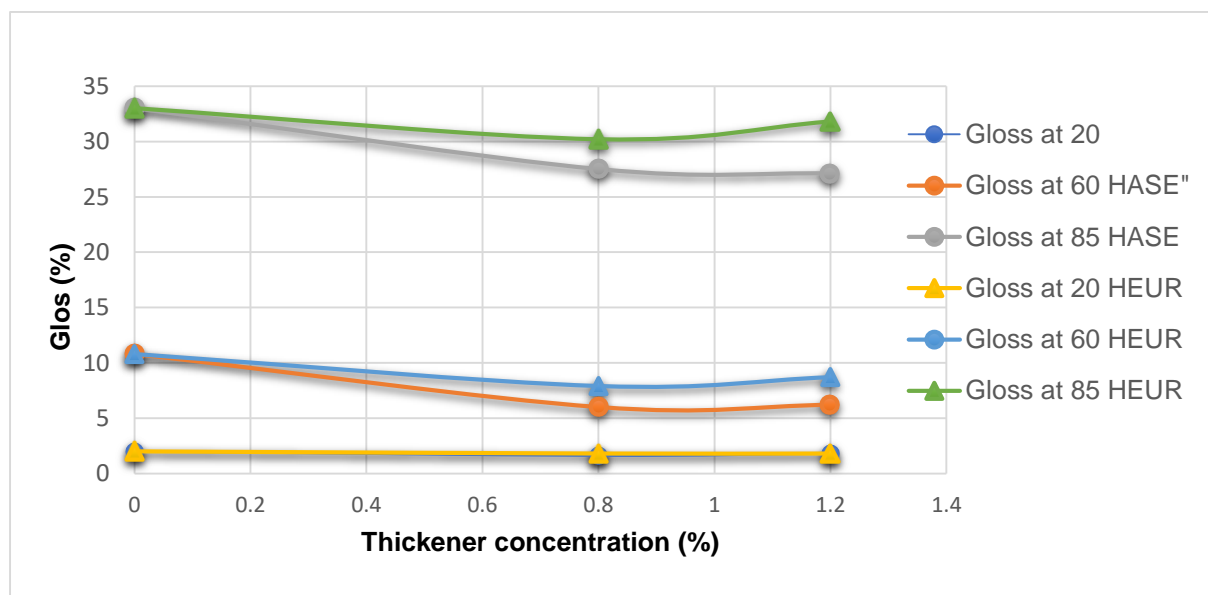


Figure 4.23: Effect of thicker type and concentration on gloss in the presence of pure acrylic binder.

Results presented in Figure 4.28 show that in the presence of pure acrylic binder, paints with HEUR rheology modifiers have higher gloss at 60° and 85° angles than HASE rheology modifiers. The gloss of a layer of paint is greatly dependent on the roughness of the surface after the paint application (Fletcher, 2002). From the rheological results, it was found that paint samples with HEUR have lower viscosities in the high shear region, which implies that it can be applied easily and hence the film will have no defect, resulting in better gloss. Samples with HASE thickener had higher viscosities throughout the shear rate range. Hence this type of paint will offer inferior application characteristics that result in brush marks after application and hence poorer gloss levels, due to surface roughness (Fletcher, 2002). A rough substrate reflects light in diverse directions, thus leading to lower gloss results (Fletcher, 2002). Gloss at a 20° angle was found not be affected by the type or concentration of the rheology modifiers.

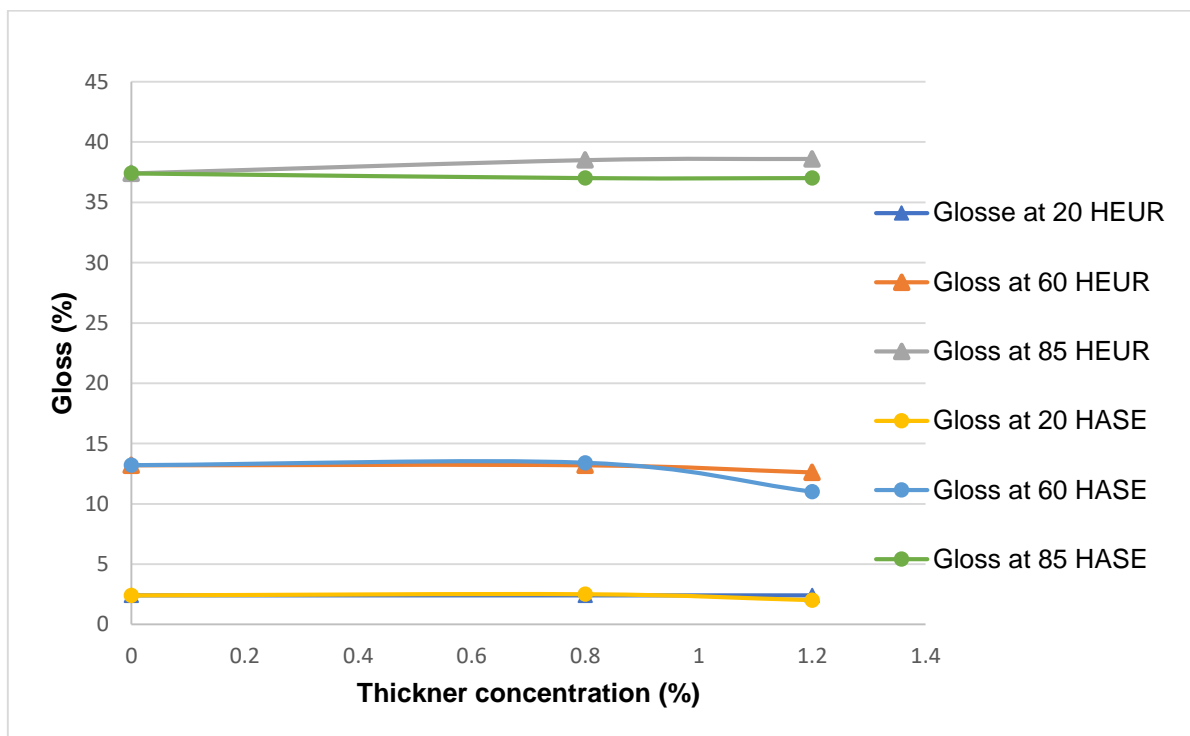


Figure 4.24: Effect of thickener type and concentration on gloss in the presence of styrene acrylic binder.

In the presence of styrene binders, there is little difference in the gloss levels produced by the two rheology modifiers, as represented in Figure 4.29. For instance, there is about a 4 percent difference in gloss at 85° between paint thickened with HASE and HEUR rheology modifiers at 0.8 percent, as well as at 1.2 percent concentration. Both rheology modifiers at concentration 0.8 percent produced comparable gloss at 60° but at 1.2 percent thickener concentration samples with HEUR were observed to have higher gloss than HASE. The 60° gloss results of paint with 1.2 percent HASE and 1.2 percent HEUR were found to be 11 percent and 12.6 percent, respectively. The reason for such slight difference in gloss produced

by paint samples containing HASE and HEUR rheology modifiers could be confirmed by the viscosity results of these samples. The flow curves in Figure 4.9 showed that, in the presence of styrene acrylic binders, there is a slight difference in the viscosities produced by these two rheology modifiers especially in the high shear rate region, the properties of film of paint is mostly dependent on its viscosity in the high rate.

4.7.2. Opacity

Table 4.17 below comprises the contrast ratio (measure of opacity) of the paint samples made of pure acrylic and styrene acrylic binders. The opacity was measured at a constant film thickness of 200µm.

Table 4.17: Opacity results in the presence of the presence of pure and styrene acrylic binder.

Thickener type & Concentration	Contrast ratio results	
	Pure acrylic	Styrene binder
0%	0.961	0.968
0.8 wt.% HEUR	0.982	0.982
1.2 wt.% HEUR	0.984	0.981
0.8 wt.% HASE	0.992	0.986
1.2 wt.% HASE	0.994	0.990

It was found that rheology modifiers can positively affect the opacity of paint. The findings showed that the sample without rheology modifiers had the lowest contrast ratio, which is the measure of opacity or hiding power, as shown in Table 4.17. For both binders, the highest opacity was found to be with the sample thickened with HASE rheology modifiers. The reason for this finding can be supported by the rheological results which suggested that the application of samples with HASE rheology modifiers results in a higher film thickness than HEUR. Higher film build implies that at the same surface area more paint containing HASE will be deposited during application and hence there is better coverage or hiding power. Even though paints with HEUR thickener produced lower contrast ratio than HASE, their opacity is acceptable because many authors confirm that any opacity above 0.98 provides full hiding (Bhavsar & Shreepathi, 2016). As the pigment concentration and the PVC were kept the same in all the experimental samples, it can be concluded that from the opacity results obtained that the binder type had a negligible effect on the opacity of paint. In this project, the film built (explained by rheological results from 3ITT and flow curves tests) was found to be a major factor affecting the opacity of paint.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1. Introduction

This study was aimed at investigating the influence that HASE and HEUR rheology modifiers have on the flow and deformation parameters of water-based paints and to correlate these rheological parameters to the properties of paints such as levelling, sagging and shelf-life stability, as well as optical properties. The performance of HASE and HEUR at various concentrations was studied in the presence of pure acrylic and styrene acrylic binders. A total of 12 experimental paint samples were prepared and subjected to rheological testing. The data obtained was then correlated to the performance of the water-based paints.

5.2. Effect of binder type

From the rheological data, it was determined that the performance of associative thickeners is greatly affected by the type of binder in the formulation (Auschra et al., 2015; Karlson et al., 2000). HASE rheology modifiers were found to have higher thickening efficiency and elasticity in the presence of pure acrylic binders, while the performance of HEUR rheology modifiers was found to be unaffected by the type of binder present in the formulation. Data from the amplitude sweep, frequency sweep and 3ITT showed that both rheology modifiers increased the elastic behaviour of paint samples, irrespective of the type of binder.

5.3. Effect of thickener concentration

The viscosity at a given shear rate and the storage modulus in the LVER of paint samples were found to increase with increases in HASE concentration. By contrast, the increase in HEUR concentration was found to result in a decrease of viscosity in the low shear region, while the high shear viscosity was found to increase with increases of HEUR concentration.

5.4. Paint stability, application, and film properties

Key properties of paint studied in this work included levelling, sagging, shelf-life stability, film thickness and ease of application.

- Paint samples thickened with HEUR rheology modifiers require less effort during application using a brush or a roller. This ease of application was suggested by the low viscosity in the high shear rate and the lower critical strain of samples containing HEUR. HASE rheology modifier, irrespective of the type of binder was observed to have higher viscosity in the high shear rate region and larger LVER. This signifies that paint samples thickened with HASE will not be applied effortlessly.

- The results obtained from all rheological tests in this study showed that none of the experimental samples experienced sagging after application.
- Paint samples containing HASE rheology modifier yielded higher film thickness during application as they had high viscosity in the high shear rate region and also high viscosity in the second interval (high shear load) of 3ITT (Bhavsar & Shreepathi, 2016).
- HEUR rheology modifiers were found to produce the best flow and levelling properties.
- High HEUR concentration was found to be detrimental to the storage stability of paint because increases in HEUR concentration led to reductions in low shear viscosity.

5.5. Optical properties

The two optical properties of paint discussed in this study included gloss and opacity or hiding power. Correlation between rheology and the optical aspects of paint was established. For example, it was found that the gloss of paint is greatly affected by the high shear rate viscosity. Lower viscosity during application leads to an adequate flow and levelling of the paint, resulting in a surface that is free of brush marks and hence provides improved gloss. Paint samples containing HEUR rheology modifier were found to have higher gloss results than paint containing HASE. A correlation between opacity, the film thickness and high shear rate viscosity in 3ITT or in flow curve tests was proven (Bhavsar & Shreepathi, 2016). Paint samples thickened with HASE rheology modifiers, were found to have higher high shear viscosities, and were also seen to possess better hiding power than HEUR rheology modifiers.

5.6. Conclusion

The core problem of this study was to establish whether rheology can be used in the study of the performance of associative rheology modifiers; upon changes such as binder type and thickener concentration, in water-based paint formulation. This study posited that rheology provided a relevant method to assess the optimisation of water-based paints formulation, as it allowed the researchers to study the deformation that paints are exposed to from the manufacturing to the application stage.

5.7. Contribution

Information is lacking on the thickening efficiency of associative rheology modifiers in the presence of various types of binders used in the production of paints. This work investigated the influence of two types of associative rheology modifiers on the flow and deformation of water-based paints: in the presence of pure acrylic and styrene acrylic binders. Furthermore, the impact of rheology on the optical properties of paints such as gloss and hiding power was studied.

5.8. Recommendations

This research highlighted the contribution of the binder type, thickener type and thickener concentration on the rheology of water-based paints. Given that formulation of paints is a complex mixture of pigments, polymeric binder, additives and water (Crawford & Meyer, 2019); a need to explore the influence of each group of raw material on the overall flow and deformation of water-based paints was revealed. For example, although considerable research has been conducted on the impact of the pigment volume concentration (PVC) on the durability of paint, information is lacking on how the PVC of paints affects their rheology.

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APPENDIX

Appendix A: Rheometer

A Discovery HR-3 Hybrid rheometer was used to conduct the rheological evaluation of water based paints. The Discovery Hybrid Rheometer (DHR) is a stress-controlled meter capable of measuring various properties such as viscosity, shear stress, loss and storage modulus, strain and phase angle. The geometries of the DHR are parallel plate (40mm) and 25/40mm 2 degree cones and cup and rotor measuring systems. The technical specifications of DHR (TA Instruments) are tabulated below.

Table A.18: Technical Specifications of the Discovery Hybrid Rheometer (TA instruments)

Specifications	DHR (HR-3)
Maximum torque	200nNm
Minimum torque	5 nNm
Torque resolution	0.05 mNm
Minimum frequency	1×10^{-7} Hz
Maximum frequency	100 Hz
Minimum angular velocity	0 rad/s
Maximum angular velocity	300 rad/s
Displacement resolution	2 nrad
Step time strain	15 ms
Step time rate	5 ms
Maximum normal force	50
Normal force sensitivity	0.005 N
Normal force resolution	0.5 mN
Bearing type, Thrust	Magnetic
Bearing type, Radial	Porous carbon

Appendix B: Manufacturing of water-based paints samples

All experimental samples were prepared in a 1 litre plastic container 11.5 cm in diameter and 12.3 cm in height. The sample preparation followed the manufacturing process of water-based paint, which involved two stages. In the mill base stage pigments and extenders were dispersed in an aqueous medium, using a high-speed mixer. During the second stage called the 'finishing stage' or 'let down', the binder or emulsions and most of the paint additives such as defoamers, thickeners and fungicides were added to the product of the mill base (pigment and extender particles dispersed in water). The later stage took place at low mixing speed.

Below is the procedure that was followed for the sample preparation.

The Mill base stage

1. The researcher weighed all the raw materials, according to the formulation.
2. In a 1 litre plastic container, container A, the correct amount (as per formulation) of the following raw materials was added:
 - Water
 - Surfactant
 - Dispersant
 - Defoamer
3. Container A was placed in the mixer and the mixer was set at between 80 and 100 rpm.
4. The correct amount of the following ingredients was added.
 - Pigment (TiO₂)
 - Extenders
5. Add slowly the content of container B (pigment and extenders) to container A, was added slowly and then the mixer speed at was set at 480 rpm. The researcher made sure that the container was firmly clamped and dispersed at high-speed mixing (480rpm) for 25 to 30 minutes.
6. The fineness of grind (FOG) test using the FOG gage was performed according to ISO1524:2000. Other tests conducted on the mixture in container A after dispersion included taking temperatures using a thermometer, Viscosity was tested using a Krebs viscometer, and pH was tested using a pH meter.

Below, the specifications and tests of the mill base are tabulated.

Table B.19: Mill base tests and specifications

Tests	Specifications
Temperature	< 40°C
F.O.G	< 30µm
Viscosity	80-100 KU (Krebs Units)
pH	8-11

7. All the mill base results were recorded, the mixer was stopped, and container A was removed from the mixer.

Let down or Finishing stage

8. In container C, the following raw materials were added, according to the amount prescribed in the formulation:

- Binder: acrylic emulsion

9. Container C was placed in the mixer, and the mixture in container A was added to container C and the mixing speed was set at 120 rpm.

10. In container D, the following raw material was added.

- Coalescent
- Defoamer
- Fungicide
- pH Adjuster

11. The contents of container D were added to container C and the mixing speed was kept at 100 rpm.

12. In a 200 ml glass beaker, the correct amount of rheology modifiers was weighed and slowly the rheology modifiers to the mixture in container C were added and the mixture was allowed to mix for 10 minutes.

N.B: When making samples without a rheology modifier step 12 must not be performed.

Appendix C: Rheological models

Linearization of the Power Law model

$$\sigma = K\dot{\gamma}^n$$

$$\text{Log } \sigma = \text{log } K + \text{log } \dot{\gamma}^n$$

$$\text{Log } \sigma = n \text{ log } \dot{\gamma} + \text{log } k$$

$$Y = mx + c$$

Plot $\text{log } \sigma$ versus $\text{log } \dot{\gamma}$ using Ms excel

Gradient = n

$$10^c = K$$

Linearization of the Hershel Bulkley model

$$\sigma = \sigma_0 + K\dot{\gamma}^n$$

$$\sigma - \sigma_0 = K\dot{\gamma}^n$$

$$\text{Log } (\sigma - \sigma_0) = \text{log } k\dot{\gamma}^n$$

$$\text{Log } (\sigma - \sigma_0) = n \text{ log } \dot{\gamma} + \text{log } K$$

$$Y = mx + c$$

Plot $\text{log } (\sigma - \sigma_0)$ vs $\text{log } \dot{\gamma}$

Gradient = n

$$10^c = K$$

Linearization of the Bingham model

$$\sigma = \sigma_0 + \eta\dot{\gamma}$$

$$\sigma = \eta\dot{\gamma} + \sigma_0$$

$$Y = mx + c$$

Plot σ vs $\dot{\gamma}$

Gradient = η

$$C = \sigma_0$$

Linearization of the Casson model

$$\sigma^{\frac{1}{2}} = \sigma_0^{\frac{1}{2}} + (n\dot{\gamma})^{\frac{1}{2}}$$

$$\sigma^{\frac{1}{2}} = n^{\frac{1}{2}}\dot{\gamma}^{\frac{1}{2}} + \sigma_0^{\frac{1}{2}}$$

$$Y = mx + c$$

Plot $\sigma^{\frac{1}{2}}$ vs $\dot{\gamma}^{\frac{1}{2}}$

Gradient = $n^{\frac{1}{2}} \therefore n = (n^{\frac{1}{2}})^2$

$$C = \sigma_0^{\frac{1}{2}} \therefore \tau = (\sigma_0^{\frac{1}{2}})^2$$

Appendix D: Paint optical properties data

Table D.20: Data of reflectance on white and black for the determination of the contrast ratio for paints made of PA binder

Thickener concentration	Reflectance on black (%)	Reflectance on white (%)	Contrast ratio
0%	0.943	0.981	0.961
0.8% HEUR	0.950	0.986	0.982
1.2% HEUR	0.966	0.989	0.984
0.8% HASE	0.982	0.990	0.992
1.2% HASE	0.985	0.991	0.994

Table D.21: Data of reflectance on white and black for the determination of the contrast ratio for paints made of PA binder

Thickener concentration	Reflectance on black (%)	Reflectance on white (%)	Contrast ratio
0%	0.951	0.983	0.968
0.8% HEUR	0.970	0.988	0.982
1.2% HEUR	0.968	0.987	0.981
0.8% HASE	0.971	0.985	0.986
1.2% HASE	0.979	0.989	0.990

Table D.22: Specular gloss raw data at 20°, 60° and 85° angles of paint samples made with PA binder

Thickener concentration	Gloss at 20° (%)	Gloss at 60° (%)	Gloss at 85° (%)
0%	2.0	10.8	33
0.8% HEUR	1.8	7.9	30.2
1.2% HEUR	1.8	8.7	31.8
0.8% HASE	1.6	6	27.5
1.2% HASE	1.8	6.2	27.1

Table D.23: Specular gloss raw data at 20°, 60° and 85° angles of paint samples made with SA binder

Thickener concentration	Gloss at 20° (%)	Gloss at 60° (%)	Gloss at 85° (%)
0%	2.4	13.2	37.4
0.8% HEUR	2.4	13.2	38.5
1.2% HEUR	2.4	12.6	38.6
0.8% HASE	2.5	13.4	37
1.2% HASE	2.0	11.0	37