

Improving engine efficiency *via* polymer shear thinning

By

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Thesis submitted to Imperial College London
For the degree of Doctor of Philosophy
And Diploma of Imperial College London (D.I.C.)

September 2016

Tribology Section
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Abstract

This thesis investigates the extent to which viscosity modifier additive shear thinning can be used to reduce hydrodynamic friction and thus improve engine efficiency while not impacting too greatly on hydrodynamic film thickness.

Novel experimental techniques are developed to measure shear-dependent viscosity over a large shear rate range.

A model hydrodynamic lubricated contact is established using a steel ball rolling/sliding against a polymer disc. This enables low contact pressures, thus avoiding significant piezoviscous effects. Novel methods are developed to measure film thickness and friction in such contacts.

Film thickness measurements on Newtonian oils in soft contacts are used to test experimentally existing soft EHL theoretical equations and to revise these. Polymer-containing oils give thinner than predicted film thickness due to shear thinning in the contact inlet induced by lubricant backflow and by the sliding speed between the rubbing surfaces. Measurements have been compared with predictions implementing existing inlet strain rate equations combined with experimental flow curves.

Theoretical equations under-predict the impact of inlet shear thinning on film thickness.

Hydrodynamic friction measurements with Newtonian oils show the expected linear dependence against sliding speed. Unfortunately, the shear stress determined from such measurements is greater than expected from theory. Despite considerable efforts, the origins of this discrepancy have not been established, which necessitates a correction factor when determining the shear stress of polymer-containing oils. Using this factor the expected reduction in hydrodynamic friction of polymer-containing oils is observed.

Overall it is found that shear thinning allows polymer-containing lubricants to produce smaller rates of increase in film thickness and friction with sliding speed in hydrodynamic lubrication than seen for Newtonian oils. Thus the slope of the Stribeck curve in the hydrodynamic regime is reduced. Hence, an oil may be designed to shear thin, adapt to the variable engine conditions and thus improve engine efficiency.

Acknowledgements

First of all, I would like to thank Professor Hugh Spikes, my supervisor for his encouragement and advice throughout the project. It was a privilege to have been exposed to his research methods and to be able to learn from his soft skills.

I am grateful to Shell for sponsoring my project and in particular to Dr. Robert Ian Taylor for the external supervision. He has always been helpful and supportive of suggestive research paths presented to him.

I would like to thank Dr. Elisabeth Marx for her inspiration and guidance in project management.

It was a great pleasure to work in the Tribology group where numerous individuals took part in organising social events and a number of group holidays in the UK, Rumania, Italy, Japan, Indonesia and in the United States of America. Luckily some of these holidays were linked to Tribology conferences and some of the discussions were work related, thank you Tribology group!

On this occasion, I would like to thank Oana Dobre, Dr. Aleks Ponjavic, Dr. Jie Zhang (Jason) and Jonathan Dench for the countless and never resting scientific debates and engineering discussions in the coffee room and round two in the pub!

Thank you to Nicusor Popescu with whom I enjoyed setting up undergraduate design projects around a formula student race car for Imperial Racing Green.

I would like to thank Dr. Colin Keyworth for his help in the Chemical Engineering department and Dr. Johan Guegan for his computer science related work.

Special thanks to all the lecturers and professors in Tribology for their time and availability. In particular Professor Daniele Dini has been supportive since my MSc.

Thank you to Dr. Neal Morgan for welcoming me in to the Shell UTC and to Dr. Mark Southby for his informative responses and supply of base oils and VMs.

A great thank you to PCS Instrument, in particular Dr. Matt Smeeth, Dr. Rich Baker and Dr. Clive Hamer for all their support and innovative design ideas.

Huge thanks to Chrissy Stevens and Mark Holloway for their super-efficiency in supporting the lab with bits and parts and orders.

Finally, I would like to thank my sister, my parents, my other relatives and friends for their moral support.

To Elisabeth

Note of the Author – declaration of originality:

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Publications arising from this work

Journal papers

- [1] Marx, N., Guegan, J., Spikes, H.A.: Elastohydrodynamic film thickness of soft EHL contacts using optical interferometry. *Tribology International* 99 pp.267-277, (2016)

Conference papers

- [1] Marx, N., Putignano, C., Guegan, J. Dini, D. Spikes, H.A.: Lubricant film thickness in compliant contacts using optical interferometry. STLE Tribology Frontiers Conference, 13-15 November 2016, Chicago, USA, (2016)
- [2] Marx, N., Guegan, J., Taylor, R.I., Spikes, H.A.: Influence of polymer shear thinning on friction and Film thickness in hydrodynamic lubricated contacts. STLE 71st Annual International Conference, 15-19 May 2016, Las Vegas, USA, (2016)
- [3] Marx, N., Guegan, J., Taylor, R.I., Spikes, H.A.: Influence of polymer shear thinning on friction in hydrodynamic lubricated contacts. 20th International Colloquium Tribology: Industrial and Automotive Lubrication, 12-14 January 2016, Stuttgart, Germany, (2016)
- [4] Marx, N., Ponjavic, A., Taylor, R.I., Spikes, H.A.: Influence of Polymer temporary shear thinning on hydrodynamic film formation and friction. STLE 70th Annual International Conference, May 17-21 2015, Dallas, USA, (2015)
- [5] Marx, N., Ponjavic, A., Taylor, R.I., Spikes, H.A.: Reducing hydrodynamic friction via polymer shear thinning. TriboUK conference, 16-17 April 2015, Loughborough, UK, (2015)
- [6] Marx, N., Taylor, R.I., Spikes, H.A.: Influence of polymer shear thinning on friction in hydrodynamic contacts. TriboBR Second International Brazilian Conference on Tribology, 3-5 November 2014, Foz do Iguau Paran, Brazil, (2014)
- [7] Marx, N., Taylor, R.I., Spikes, H.A.: Influence of polymer shear thinning on friction in hydrodynamic contacts. STLE 69th Annual International Conference, 18-22 May 2014, Orlando, USA, (2014)

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List of equations

$$\dot{\gamma} = \frac{V}{h} \quad (1.1)$$

$$\eta = e^{A + \frac{B}{C+T}} \quad (2.1)$$

$$VI[\%] = \frac{L-U}{L-H} \times 100 \quad (2.2)$$

$$\log(v) = \log(v_{base}) + k_1 M_w \quad (2.3)$$

$$\log(v) = \log(v_{base}) + k_2 C_{\%} \quad (2.4)$$

$$v_{th} = k C_{\%}^a \times M_w^b \quad (2.5)$$

$$\eta_{red} = \frac{\eta_{sp}}{C_{\%}} \quad (2.6)$$

$$\eta_{sp} = \eta_{rel} - 1 \quad (2.7)$$

$$\eta_{rel} = \frac{\eta}{\eta_{base}} \quad (2.8)$$

$$< R_g^2 >_w^{0.5} / nm = 0.023 M_w^{0.54} \quad (2.9)$$

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + p\dot{\gamma}^q} \quad (3.1)$$

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})(1 + (\lambda\dot{\gamma})^2)^{(n-1)/2} \quad (3.2)$$

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})(1 + (\lambda\dot{\gamma})^a)^{\frac{n-1}{a}} \quad (3.3)$$

$$\frac{\eta}{\eta_0} = \frac{1+d\tau}{1+c\tau} \quad (3.4)$$

$$\eta = \frac{j(1-\exp(-i\dot{\gamma}))}{\dot{\gamma}} + k \quad (3.5)$$

$$\frac{\eta}{\eta_0} = \frac{1+f\tau \times \exp\left(\frac{h}{T}\right)}{1+g\tau \times \exp\left(\frac{h}{T}\right)} \quad (3.6)$$

$$\frac{\eta}{\eta_0} = \frac{\eta_\infty}{\eta_0} + \frac{\left(1-\frac{\eta_\infty}{\eta_0}\right)\left(1-\exp\left(-l\dot{\gamma}\exp\left(\frac{m}{T}\right)\right)\right)}{l\dot{\gamma}\exp\left(\frac{m}{T}\right)} \quad (3.7)$$

$$\frac{\eta}{\eta_0} = \frac{\eta_\infty}{\eta_0} + \frac{1-\eta_\infty/\eta_0}{1+\text{antilog}\left(u+q\log(\dot{\gamma})+\frac{s}{T}\right)} \quad (3.8)$$

$$\eta_{sp} = \frac{\eta-\eta_{base}}{\eta_{base}} \quad (3.9)$$

$$SSI = \frac{\nu-\nu_\infty}{\nu_0-\nu_\infty} \quad (3.10)$$

$$SSI = \frac{1}{1+p\dot{\gamma}^q} \quad (3.11)$$

$$SSI = \frac{1-\exp(-l\dot{\gamma}e^{m/T})}{l\dot{\gamma}e^{m/T}} \quad (3.12)$$

$$PE = \frac{\text{experimental } \Delta h_c}{\text{predicted } \Delta h_c} \quad (3.13)$$

$$\text{experimental } \Delta h_c = \frac{h_c(\text{blend})-h_c(\text{base oil})}{h_c(\text{base oil})} \quad (3.14)$$

$$\text{predicted } \Delta h_c = \frac{\eta(\text{blend})^{0.67}-\eta_{base}^{0.67}}{\eta_{base}^{0.67}} \quad (3.15)$$

$$\eta = \eta_0 e^{\alpha \bar{P}} \quad (3.16)$$

$$\eta = m \left(\frac{\partial u}{\partial z} \right)^{n-1} \quad (3.17)$$

$$\text{isoviscous-rigid, } H_c = H_0 = 140 \quad (5.1)$$

$$\text{piezoviscous-rigid, } H_c = H_0 = 5.35g_v^{0.375} \quad (5.2)$$

$$\text{isoviscous-elastic, } H_c = 5.08g_E^{0.67}, H_0 = 3.28g_E^{0.67} \quad (5.3)$$

$$\text{piezoviscous-elastic } H_c = 2.55 g_v^{0.53} g_E^{0.13}, H_0 = 1.69 g_v^{0.49} g_E^{0.17} \quad (5.4)$$

$$H_c = H_0 = \left(\frac{h_{c/0}}{R'_x} \right) \left(\frac{\bar{W}}{\bar{U}} \right)^2 \quad (5.5)$$

$$g_v = \frac{\bar{G} \bar{W}^3}{\bar{U}^2} \quad (5.6)$$

$$g_E = \frac{\bar{W}^{8/3}}{\bar{U}^2} \quad (5.7)$$

$$\bar{U} = \frac{U_e \eta_0}{E' R'_x} \quad (5.8)$$

$$\bar{W} = \frac{W}{E' R_x'^2} \quad (5.9)$$

$$\bar{G} = \alpha E' \quad (5.10)$$

$$\frac{1}{R'_x} = \frac{1}{R_{x1}} + \frac{1}{R_{x2}} \quad (5.11)$$

$$\frac{2}{E'} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \quad (5.12)$$

$$\frac{h_c}{R'_x} = 5.08 \bar{U}^{0.66} \bar{W}^{-0.21}, \frac{h_0}{R'_x} = 3.28 \bar{U}^{0.66} \bar{W}^{-0.21} \quad (5.13)$$

$$\frac{h_c}{R'_x} = 3.3 \bar{U}^{0.64} \bar{W}^{-0.22}, \frac{h_0}{R'_x} = 2.8 \bar{U}^{0.66} \bar{W}^{-0.21} \quad (5.14)$$

$$H_0(\text{exit}) = 2.83 g_E^{0.7} \quad (5.15)$$

$$H_0(\text{side}) = 8.55 g_E^{0.625} \quad (5.16)$$

$$H_c = 3.56 g_E^{0.7} \quad (5.17)$$

$$\frac{h_c(\text{exit})}{R'_x} = 2.83 \bar{U}^{0.6} \bar{W}^{-0.13} \quad (5.18)$$

$$\frac{h_c(side)}{R'_x} = 8.55\bar{U}^{0.75}\bar{W}^{-0.23} \quad (5.19)$$

$$\frac{h_c}{R'_x} = 3.56\bar{U}^{0.6}\bar{W}^{-0.13} \quad (5.20)$$

$$T' = \frac{\lambda'}{2n'} \quad (5.21)$$

$$H_c = \left(\frac{h_c}{R'_x}\right) \left(\frac{\bar{W}}{\bar{U}}\right)^2 = 5.08g_E^{0.67} \quad (5.22)$$

$$H_c = \left(\frac{h_c}{R'_x}\right) \left(\frac{\bar{W}}{\bar{U}}\right)^2 = 2.7g_E^{0.725} \quad (5.23)$$

$$H_0(exit) = \left(\frac{h_0(exit)}{R'_x}\right) \left(\frac{\bar{W}}{\bar{U}}\right)^2 = 2.1g_E^{0.725} \quad (5.24)$$

$$H_0(side) = \left(\frac{h_0(side)}{R'_x}\right) \left(\frac{\bar{W}}{\bar{U}}\right)^2 = 2.9g_E^{0.69} \quad (5.25)$$

$$\dot{\gamma} = \frac{SRR \times U_e}{h_c} \quad (6.1)$$

$$\tau = COF \times \bar{P} \quad (6.2)$$

$$\tau = \eta_{in-contact} \times \dot{\gamma} \quad (6.3)$$

$$\eta_{in-contact} = \eta_{atm} \times e^{\alpha\bar{P}} \quad (6.4)$$

$$F = \int_a^{na} 2\pi r \tau \, dr \times \frac{2}{3} \quad (6.5)$$

$$\tau = \eta_0 \frac{V}{h} \quad (6.6)$$

$$\dot{\gamma}_{inlet}(PR) = \frac{3}{2} \frac{U_e}{h_c} \quad (8.1)$$

$$\dot{\gamma}_{inlet}(SRR) = \frac{(3+\frac{SRR}{2})^2}{6} \frac{U_e}{h_c} \quad (8.2)$$

$$\eta_{inlet} = \frac{E'R'_x}{U_e} \times \left(\frac{h_c}{2.7\bar{R}\left(\frac{W}{E'R_x'^2}\right)^{\left(0.75\times\frac{8}{3}-2\right)}} \right)^{1/(2-2\times 0.725)} \quad (8.3)$$

$$\dot{\gamma}_{inlet} = \frac{1}{A} \left(\left(\frac{\eta_{inlet}-\eta_{base}}{\eta_0-\eta_{base}} \right)^{\frac{a}{n-1}} - 1 \right)^{1/a} \quad (8.4)$$

$$\tau = \dot{\gamma} \times \eta(\dot{\gamma}) \quad (8.5)$$

$$\eta_{atm} = \eta_{base} + (\eta_0 - \eta_{base}) \times \left(1 + (A'\tau)^{a'} \right)^{(n'-1)/a'} \quad (8.6)$$

$$\tau = \dot{\gamma} \times \eta_{atm}(\dot{\gamma}) \times e^{\alpha\bar{P}} \quad (8.7)$$

Nomenclature

α	= Pressure viscosity coefficient	ν_0	= Kinematic zero shear viscosity
$\dot{\gamma}$	= Shear rate	ν_∞	= Kinematic infinite shear viscosity
η	= Dynamic viscosity	ν_{base}	= Kinematic viscosity of the base oil
η_0	= Dynamic zero shear viscosity	ν_{th}	= Theoretical kinematic viscosity
η_{atm}	= Sheared dynamic viscosity at atmospheric Pressure	ν	= Poisson's ratio
$\eta_{in-contact}$	= Sheared dynamic viscosity in the centre of the contact	ν_1, ν_2	= Poisson's ratio of the two solid bodies
η_{inlet}	= Sheared viscosity at the inlet of the contact	τ	= Shear stress
η_∞	= Dynamic infinite shear viscosity	$C_\%$	= Concentration
η_{base}	= Dynamic viscosity of the base oil	F	= Frictional force
η_{red}	= Reduced dynamic viscosity	E	= Young's modulus
η_{rel}	= Relative dynamic viscosity	E'	= Reduced elastic modulus
η_{sp}	= Specific dynamic viscosity	E_1, E_2	= Young's moduli of the two solid bodies
λ'	= Wavelength	h	= Film thickness
ν	= Kinematic viscosity	$h_{c/0}$	= Central and minimum film thickness
		h_c	= Central film thickness
		h_0	= Minimum film thickness

H	= Kinematic viscosity of the Pennsylvanian oil at 40°C	$< R_g^2 >_w^{0.5}$	= Weight-average root- mean-square of gyration
H_c	= Non dimensional central film thickness	R'_x	= Reduced radius
H_0	= Non dimensional minimum film thickness	R_{x1}, R_{x2}	= Radii of the two solid bodies
L	= Kinematic viscosity of the Gulf Coast oil at 40°C	T	= Temperature
		T'	= Difference in film thickness between two consecutive fringe peaks
M_w	= Molecular weight	U	= Kinematic viscosity of the tested oil 40°C
n'	= Refractive index		
$\bar{P}$	= Mean pressure	U_e	= Entrainment speed
R	= Radius of the ball	V	= Sliding speed
		W	= Load

Abbreviations

<i>COF</i>	= Coefficient of friction	<i>PDMS</i>	= polydimethylsiloxane
<i>CY</i>	= Carreau Yasuda equation	<i>PE</i>	= Polymer efficiency
<i>DBP</i>	= Dibutylphthalate	<i>PH</i>	= Phenoxazone
<i>DEHP</i>	= Diethylhexylphthalate	<i>PIP</i>	= Polyisoprene
<i>DMP</i>	= Dimethylphthalate	<i>PR</i>	= Pure rolling
<i>EHD</i>	= Elastohydrodynamic	<i>PS</i>	= Polystyrene
<i>EHL</i>	= Elastohydrodynamic lubrication	<i>PU</i>	= Polyurethane
<i>GPC</i>	= Gel Permutation Chromatography	<i>PM</i>	= Pyrromethane
<i>HSD</i>	= Hydrogenated styrene diene	<i>PMA</i>	= Polymethacrylate
<i>HTHS</i>	= High temperature high shear rate dynamic viscosity, η at $10^6 s^{-1}$ at $150^\circ C$	<i>PMMA</i>	= Polymethyl- methacrylate
<i>LIF</i>	= Laser induced fluorescence	<i>SRR</i>	= Slide-to-roll ratio
<i>MTM</i>	= Mini traction mashine	<i>SSI</i>	= Shear stability index
<i>nDOP</i>	= n-dioctylphthalate	<i>SVM</i>	= Stabinger viscometer
<i>OCF</i>	= Olefin-copolymer	<i>Th.</i>	= Theoretically (calculated film thickness)
<i>PC</i>	= Polycarbonate	<i>THF</i>	= Tetrahydrofuran
		<i>USV</i>	= Ultra shear viscometer
		<i>VI</i>	= Viscosity index
		<i>VM</i>	= Viscosity modifier

1 Introduction

This chapter introduces the importance of improving engine efficiency in passenger vehicles. Reducing friction in the engine is a neat solution since it is easily applicable to already produced cars. Engine oil shear thinning is suggested as key to unlock improved fuel economy. Shear thinning potentially transforms an oil into an intelligent lubricant that could adapt to the different contact conditions it experiences in the engine.

This chapter also outlines how the investigation of lubricant shear thinning is approached experimentally in this thesis.

1.1 BACKGROUND TO IMPROVING ENGINE EFFICIENCY

Over the past decade the greenhouse effect resulting from a build up of CO_2 in the atmosphere has become an increasing concern. Since 1990 CO_2 emissions have increased by 18% in the United States alone and 28% of the total U.S. CO_2 emission originates from transportation [1]. Since the automobile is today's main mode of transportation in many countries, it is of utmost importance that its emissions are reduced. Governments have therefore set norms for the automotive industry. Europe's targets are the most ambitious, having required a decrease of CO_2 emissions of passenger vehicles to 130g/km by 2015 and mandating a fall to 95g/km by 2020. Automotive manufacturers failing to achieve these results face financial penalties.

The principle way to reduce emissions is to increase the energy efficiency of vehicles so that they consume less fuel. There are many ways to do this, including reducing the mass of vehicles, changing the way that vehicles are driven, and introducing more efficient engine designs. One very important approach is to reduce mechanical losses by reducing friction.

Mechanical losses occur in all moving components in a vehicle, including the engine, transmission and tyres. However, friction in the engine is the highest mechanical loss factor according to K. Holmberg et al. [2], consuming no less than 11.5% of the total fuel energy of a passenger vehicle. Most of this loss (80%) occurs in the hydrodynamic

lubrication (HL) of engine bearings and seals and in the elastohydrodynamic lubrication (EHL) of piston-cylinder sliding and cam-follower sliding contacts [3-5]. An improvement in this aspect of vehicles would result in significant and highly beneficial emissions reduction.

This project will investigate the improvement of engine efficiency by reducing friction in hydrodynamic lubrication via oil design rather than changing the design of the individual mechanical components.

“The lower the viscosity in the lubricant, the less fuel an engine needs to overcome its resistance” says S. Gunsel, Vice President of Global Commercial Technology at Shell.

To minimise hydrodynamic friction the oil viscosity thus needs to be minimized. At the same time the viscosity needs to be high enough to build up sufficiently thick lubricant films to protect the engine components. This is classically illustrated by the Stribeck curve as illustrated in figure 1.1 where V is the sliding speed and P the load on the lubricated contact.

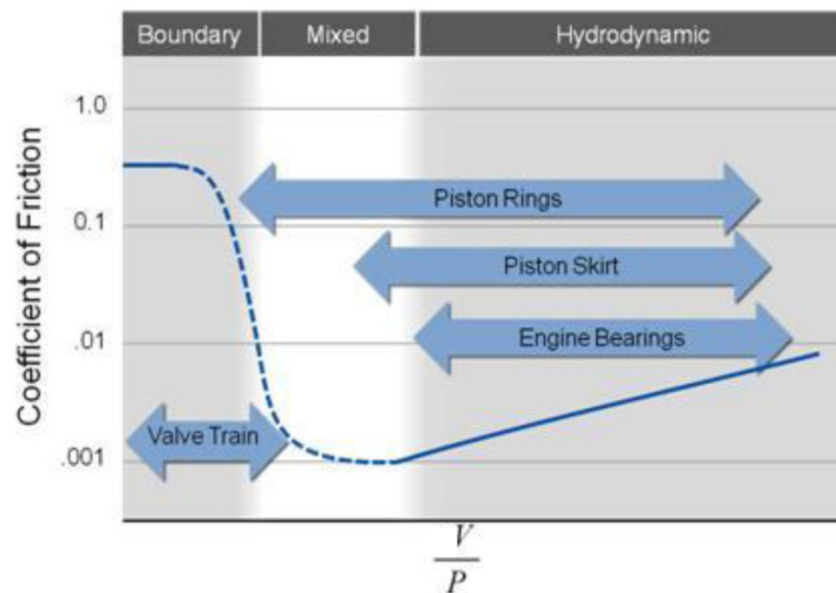


Fig. 1.1: Engine components placed on a Stribeck curve for Newtonian oils [6]

The choice of engine oil viscosity is complicated by the fact that a single oil must lubricate several components at the same time, including the bearings, piston/liner, seals and cams. This means the oil is subject to different working conditions in different components so that the oil properties chosen have to be a compromise to work well in all components. A further complication is that crankcase engines operate over a cycle, which results in the components being subject to fluctuating conditions, especially of speed and load. This leads to a conundrum since at low speed and high loads a high viscosity oil is needed to build a hydrodynamic film able to separate the rubbing surfaces and prevent wear. However, at high sliding speeds a high viscosity oil will lead to a film being formed that is thicker than required and therefore has unnecessarily high hydrodynamic friction. The ideal oil would have high viscosity at low speeds and high loads but low viscosity at high speeds and low loads so as to maintain the minimum necessary hydrodynamic film thickness to separate the rubbing surfaces and the minimum possible friction regardless of speed or load.

This is practically impossible with a Newtonian oil but one way to partially achieve it is to use the temporary shear thinning properties of the lubricant as an oil design parameter. The ideal oil in this context can be envisaged as one whose viscosity reduces due to shear thinning as entrainment speed increases so as to maintain a fixed film thickness and friction over the whole speed range. Figure 1.2 shows how such a shear thinning oil could affect the Stribeck curve.

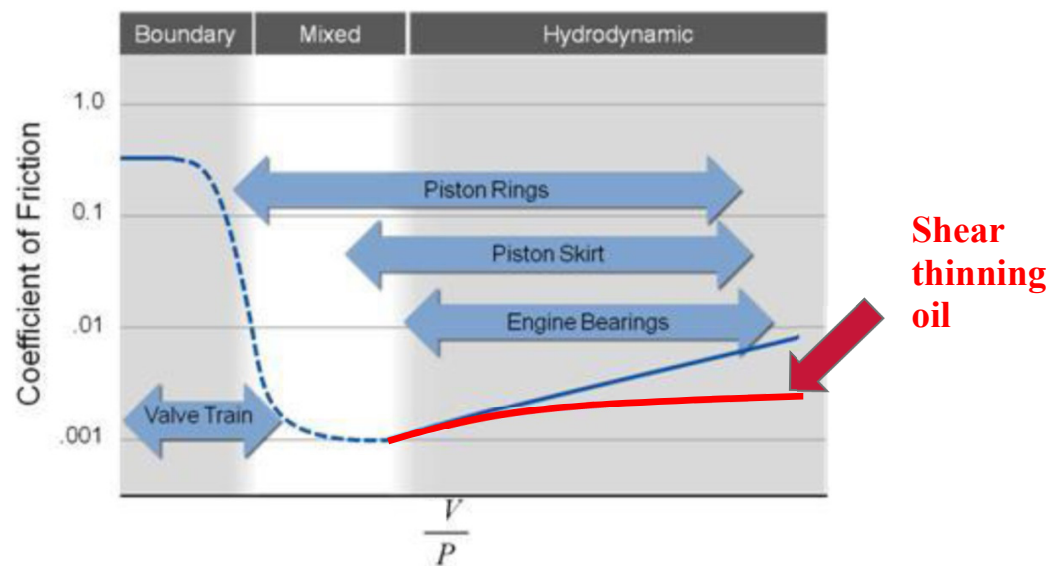


Fig. 1.2: Possible effect of shear thinning oils on the Stribeck curve

Simple base fluids are Newtonian and so do not shear thin. However almost all existing engine oils already contain polymeric viscosity modifiers that have the ability to shear thin. Realising and commercialising a shear thinning adjustable oil optimised to reduce friction is thus tangible.

The goal of this project is to explore the influence of lubricant shear thinning on hydrodynamic film thickness and friction in order to show that this approach is, at least in part, feasible.

1.2 PROJECT OUTLINE

Most modern engine lubricants contain polymer additives in order to improve the viscosity index of the blend. These polymer solutions shear thin at high strain rates.

Until quite recently it was generally considered that this shear thinning behaviour was undesirable since it leads to thinner oil films and thus possible wear and scuffing in hydrodynamic lubricated contacts. The possibility that shear thinning might lead to lower friction was recognised in the mid 1980s but does not appear to have been systematically exploited as a design tool until very recently. In consequence, experimental research is quite limited. One major problem has been the difficulty of

obtaining accurate measurements of viscosity at high shear rates and in particular over the wide range of shear rates present in engines.

For films in Couette flow, as predominantly present in sliding contacts, shear rate is defined by the ratio of the velocity difference between the two bounding surfaces V , and the separation between them, h , as shown in Eq. 1.1.

$$\dot{\gamma} = \frac{V}{h} \quad (1.1)$$

It is currently quite easy to obtain single measurements of viscosity at a set shear rate of 10^6 s^{-1} using standard ASTM test methods, but much less straightforward to obtain measurements at higher shear rates or, indeed, between 10^4 and 10^6 s^{-1} . The first goal of this project is therefore to obtain viscosity measurements over a wide shear rate range of polymer containing blends. The results of these *flow curves* will then be used to help select lubricants with properties that may enable reduced friction.

The experimental range of shear rates sought is 10^1 to 10^7 s^{-1} . No single setup is, however, able to measure the complete range since it is not possible to accurately vary speeds and separations between surfaces and obtain a ratio of more than a factor of 100 while still maintaining a high sensitivity in the shear force measuring sensor. It is, however, possible to produce a series of test rigs able to cover smaller shear rate ranges and combine these to span the whole required shear rate range.

In the past, viscosity measurements were limited by shear heating and could thus only reach 10^6 s^{-1} , and even at that shear rate only low viscosity oils could be tested. However, this limiting shear rate has recently been extended to 10^7 s^{-1} using a system that minimises and accounts for residual shear heating. This is commercialised by PCS Instruments (Acton, UK) as instrument called the “Ultra Shear Viscometer (USV)” and is employed in this study to measure viscosity in the shear rate range 10^6 to 10^7 s^{-1} . A commercially available rheometer is used to accurately measure viscosity from low shear rates up to 10^4 s^{-1} . For the mid shear rate range 10^4 to 10^6 s^{-1} a novel, large gap geometry is developed based on the USV. These three experimental setups are

calibrated with reference to the SVM 3000 (Stabinger Viscometer, precision according to ASTM standard).

While reversible or *temporary shear thinning* may enable improved engine efficiency, high shear rates and stresses can also cause the polymer chains to permanently break resulting in the phenomenon known as *permanent shear thinning*. This is generally undesirable since it causes the lubricant to fall below its original design viscosity. Permanent shear thinning is not the main topic in this thesis but nevertheless, methods to account for and eliminate permanent shear thinning in the flow curves are needed to ensure reliable measurements of temporary shear thinning and are therefore presented and used throughout this thesis.

A second challenge faced in this study is to develop a suitable hydrodynamic contact in which the effect of lubricant shear thinning on film thickness and friction can be investigated. It is experimentally quite difficult to set up a thin film hydrodynamic, flat-on-flat contact since this requires a test apparatus with very good alignment and large loads. Instead, the innovative approach of using a deformable polymer ball on glass disc contact and a steel ball on polymer disc contact has been developed. It is not possible to polish polymer surfaces to a smooth finish so one problem to be overcome was to achieve extremely low roughnesses, preferably below 10 nm. Some materials as well as production methods enabling these roughnesses had to be researched.

The conventional method of measuring film thickness in a soft contact is laser induced fluorescence but despite considerable work by the author this was found not to have the required accuracy. Instead optical interferometry, which is normally used to study film thickness in hard contacts was developed for use in soft contact conditions. This technique was first tested and validated using Newtonian oils and then employed to study polymer-containing solutions.

The use of soft contacts to ensure hydrodynamic conditions was then extended to measure friction by employing polymer discs in a rolling-friction machine. Although an obvious extension, this has not been done before in the context of studying hydrodynamic lubrication.

Finally, based on measured shear thinning flow curves, hydrodynamic film thickness and hydrodynamic friction measurements, existing hydrodynamic models are validated using the shear thinning lubricants and the possibility of improving engine efficiency *via* temporary shear thinning is examined.

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2 Viscosity modifiers

This chapter reviews published work on viscosity modifiers. Viscosity modifier (VM) type, molecular weight, concentration and the base oil properties in which the VM is diluted all play a role in engine lubrication. Engine efficiency is improved by the reduced temperature dependency of viscosity a VM provides.

2.1 PURPOSE OF VISCOSITY MODIFIERS

All liquids show a decrease in viscosity with increasing temperature. For very low viscosity liquids this decrease is exponential but for higher viscosity ones such as many lubricants, viscosity falls faster than exponentially with temperature, as indicated by the widely used Vogel viscosity-temperature Eq. 2.1.

$$\eta = e^{A + \frac{B}{C+T}} \quad (2.1)$$

From Eq. 2.1 it can be seen that it is not possible to quantify the viscosity temperature dependence of lubricants over a finite temperature range by just one constant. However, despite this, the use of a single value descriptor of viscosity-temperature dependence is still appealing for its simplicity and ease of use and this led Dean and Davis in 1929 to develop the concept of the viscosity index (VI) [1].

A VI of 0 was attributed to the highest temperature-dependent mineral oil at the time, which was the oil coming from the Gulf Coast and a VI of 100 to describe the oil with the lowest fall in viscosity with temperature, which was the oil from Pennsylvania. Since for most applications it is desirable that viscosity does not fall too much with temperature, higher VIs were (and are) generally considered desirable.

In order to calculate the VI of an oil the following formula was developed implementing reference kinematic viscosities at 100°C and the kinematic viscosity at 40°C of the tested oil:

$$VI[\%] = \frac{L-U}{L-H} \times 100 \quad (2.2)$$

where L is the kinematic viscosity of the Gulf Coast oil at 40°C, H is the kinematic viscosity of the Pennsylvanian oil at 40°C and U is the Kinematic viscosity of the tested oil 40°C.

Improvements in refining methods for mineral oils as well as the development of synthetic oils has led to the development of base oils having VIs considerably higher than 100 since 1929. Nevertheless the essential concept of VI has not changed, although it has been modified to accommodate very high VI oils [2]. Following the ASTM 2270 procedure becomes slightly more complicated than Eq. 2.2. Reference kinematic viscosities are calculated from an input value read in a table which depends on the measured oil viscosity at 100°C. Furthermore, the equation choice is condition based on whether the kinematic viscosity at 40°C of the tested oil is greater or smaller than the kinematic viscosity of the reference oil at 100°C.

Lubricant temperature dependency is a particular issue for engine lubrication. On the one hand, when an engine starts up, especially in winter, all components including the oil are cold. The oil must thus have a low enough viscosity in order to flow and effectively lubricate the highly loaded moving components. On the other hand, when an engine is run over a longer period of time, especially at high power, it becomes hot. Because of the engine cooling system the bulk lubricant stabilises slightly below 100°C but within the pistons and bearings it can be considerably higher. This leads to a reduction in viscosity, which, if too great, may result in excessive wear or scuffing.

In the early decades of the twentieth century this problem was addressed by changing the engine oil between Winter and Summer and using a lower viscosity oil grade in Winter. In the late 1930s it was found that the VI of engine oils could be increased by adding small proportions of high molecular weight polymer additives [3]. The main initial purpose of this was to reduce oil consumption at high temperatures but by 1947 it was realised that some polymers enabled so called “double branded” engine oils to

be developed, i.e. those that could meet the requirements of both winter and summer grades [4]. Nowadays almost all engine oils are “multigrade” and this is achieved by using polymer additives that are now known as “viscosity index improvers” (VIIs) or “viscosity modifiers” (VMs).

2.2 TYPES OF VISCOSITY MODIFIERS

Over the last 70 years many polymers have been tested for their ability to both improve the viscosity index and survive the harsh conditions experienced in the automotive lubrication environment. However, nowadays three groups of polymeric viscosity modifiers have become widely used, olefin-copolymers, hydrogenated styrene-diene polymers and polymethacrylates.

2.2.1 OLEFIN-COPOLYMERS

Olefin-copolymers (OCP) are linear branched polymers, usually containing 40-60% by weight of ethylene with the remaining per cent being propylene. These polymers feature a strong viscosity thickening ability and are cheap to manufacture [5-7].

It is important to obtain the correct ratio of ethylene to propylene molecules. Too high a proportion of ethylene molecules can lead to the polymer not being soluble in hydrocarbon base oils, in particular at low temperature. Too many propylene molecules can lead to too easy oxidation [5].

The chemical structure for typical olefin copolymers is shown in figure 2.1.

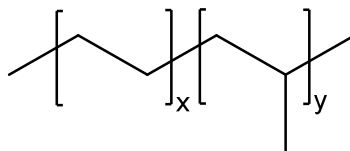


Fig. 2.1: Olefin copolymer, random copolymer of ethylene and propylene

2.2.2 HYDROGENATED STYRENE-DIENE POLYMERS

Hydrogenated styrene-diene polymers are copolymers of styrene and a diene. Since the diene has two double bonds, one is left during polymerisation and, since this would lead to the polymer being easily oxidised, it has to be hydrogenated. This type of polymer molecule can be grown in a quite controlled fashion, leading to the possibility of complex polymer architectures such as star polymers. This enables the shear stability and thickening power to be manipulated [6]. Two types of diene are commonly used, isoprene and butadiene. A styrene-butadiene polymer is made from 50-60% of styrene by weight with the remaining per cent butadiene.

Different example chemical structures for hydrogenated styrene diene block polymers may be found in figures 2.2-2.5. Hydrogenated styrene-diene also comes as star polymer as shown in figure 2.6.

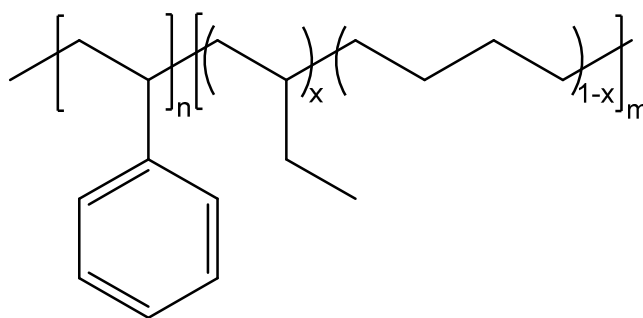


Fig. 2.2: Hydrogenated styrene butadiene block copolymer, mixture of 1,4 and 1,2 addition

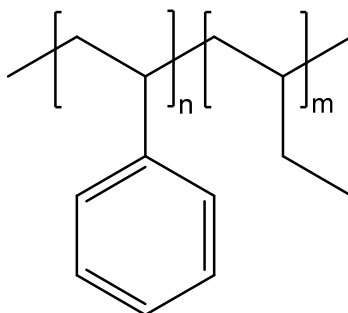


Fig. 2.3: Hydrogenated styrene butadiene block copolymer, 1,2 addition

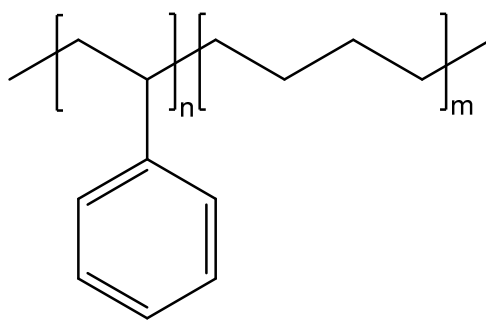


Fig. 2.4: Hydrogenated styrene butadiene block copolymer, 1,4 addition

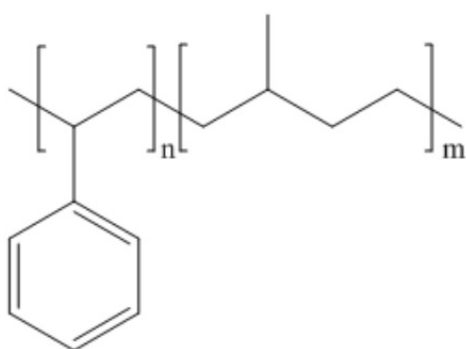


Fig. 2.5: Example of a hydrogenated styrene isoprene block copolymer

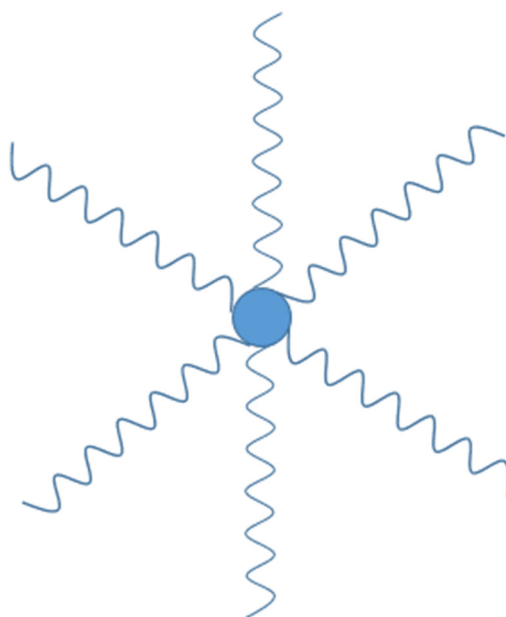


Fig. 2.6: Example of a hydrogenated styrene star polymer

2.3 EFFECT OF CONCENTRATION AND MOLECULAR WEIGHT

Concentration and molecular weight of VIIs have a strong impact on the viscosity of their blends. An increase in either increases viscosity of the blend, but it was soon found that very high molecular weights were highly fragile so that their thickening power was lost over time. Typical molecular weights in today's engine oils are between 100k and 600k g/Mol depending on the polymer architecture. They are used at neat polymer concentrations of typically 0.5% to 3% wt., depending on polymer type and application.

Fuks *et al* [9] suggested two viscosity thickening laws at low shear rate:

(i) a molecular weight dependence:

$$\log(\nu) = \log(\nu_{base}) + k_1 M_w \quad (2.3)$$

(ii) a concentration dependence:

$$\log(\nu) = \log(\nu_{base}) + k_2 C_{\%} \quad (2.4)$$

Kaplan *et al* [10] proposed the combined law:

$$\nu_{th} = k C_{\%}^a \times M_w^b \quad (2.5)$$

k_1, k_2, k, a and b being constants

Bartz [11] shows experimentally the correspondence of molecular weight and concentration in order to obtain a same viscosity oil at 100°C (figure 2.8). He also showed the linear dependency of specific viscosity versus concentration for different PMAs (figure 2.9) where specific viscosity is defined in Eq. 2.7.

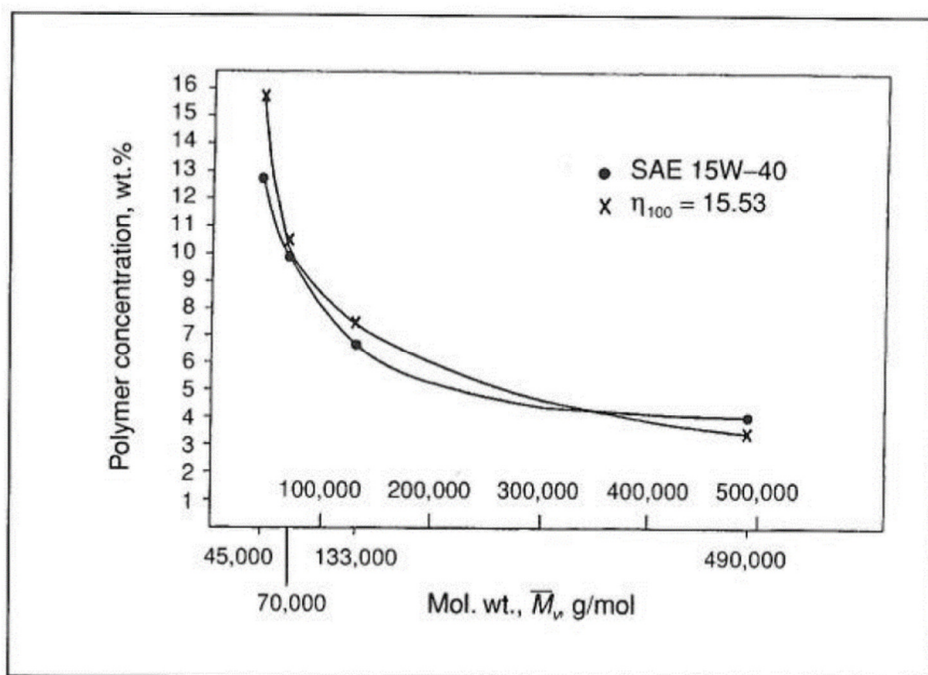


Fig. 2.8: Correspondence of molecular weight and concentration in order to obtain a same viscosity lubricant for SAE 15W-40 and $\eta_{100} = 15.53$ oils [11]

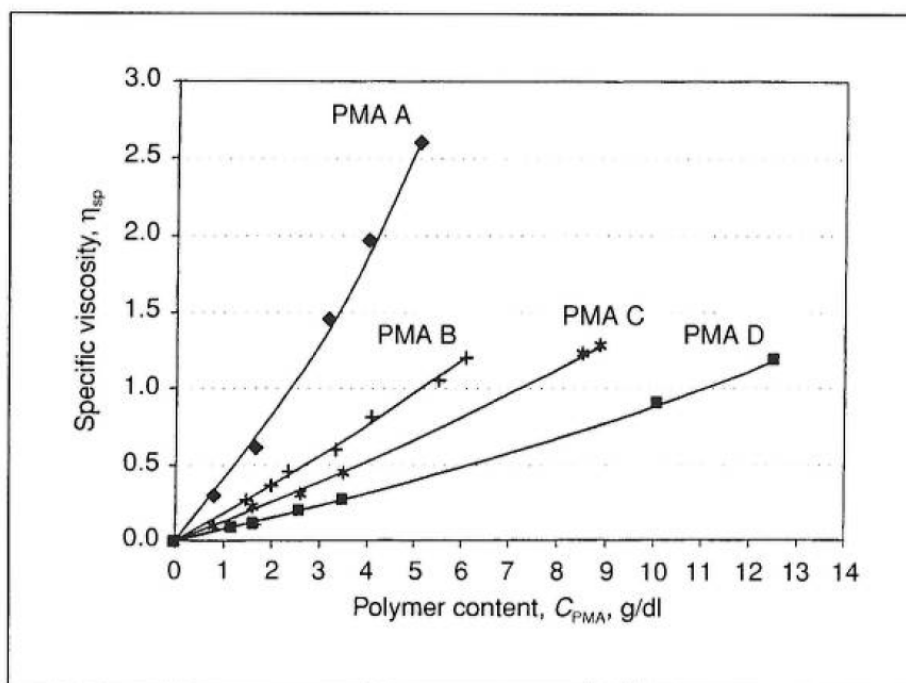


Fig. 2.9: Specific viscosity at 100°C versus concentration of polymer content for different PMA polymers [11]

2.4 TEMPERATURE DEPENDENCE OF VISCOSITY MODIFIER THICKENING

Stamgbaugh [8] categorises Mueller's [12] temperature and concentration dependency for the three major types of polymers in figure 2.10. Reduced viscosity is defined in Eq. 2.6.

$$\eta_{red} = \frac{\eta_{sp}}{C_{\%}} \quad (2.6)$$

where η_{sp} is the specific viscosity, c the concentration and η_{rel} the relative viscosity defined by;

$$\eta_{sp} = \eta_{rel} - 1 \quad (2.7)$$

$$\eta_{rel} = \frac{\eta}{\eta_{base}} \quad (2.8)$$

η is the viscosity of the polymer solution while η_{base} is the viscosity of the polymer-free solvent which might be base oil or, for a formulated oil, the base oil plus non-polymer additives.

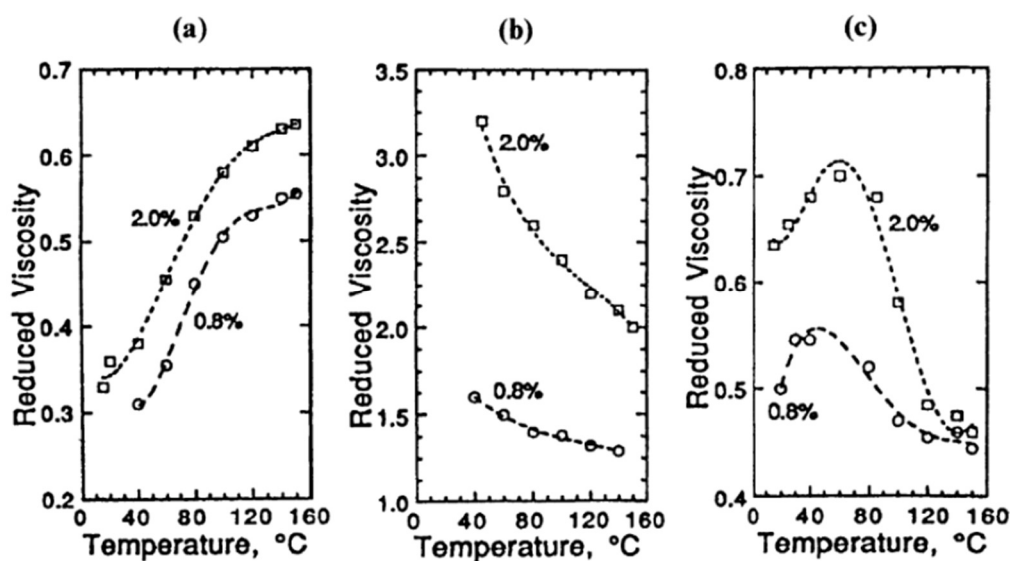


Fig. 2.10: Temperature dependence of different VMs: (a) PMA, (b) OCP, (c) HSD [8,12]

It is evident that the thickening behaviour is very different for the different polymer types, with thickening increasing with temperature for PMA, falling with temperature for OCP and showing a maximum at intermediate temperature for styrene-diene. LaRiviere et al [13,15] and Warren et al [14] investigated in detail the temperature dependency of four VMs an olefin copolymer, a polymethacrylate, a hydrogenated diene copolymer and a dispersant olefin copolymer. Viscosity and density were varied by blending VMs at a range of concentrations and making measurements at several temperatures. It was found that PMA was the only VM amongst the four that increased its contribution to viscosity with increasing temperature as illustrated in figure 2.11 [15]. However, its total intrinsic viscosity contribution was much lower [14]. These results are in harmony with Mueller's findings [12].

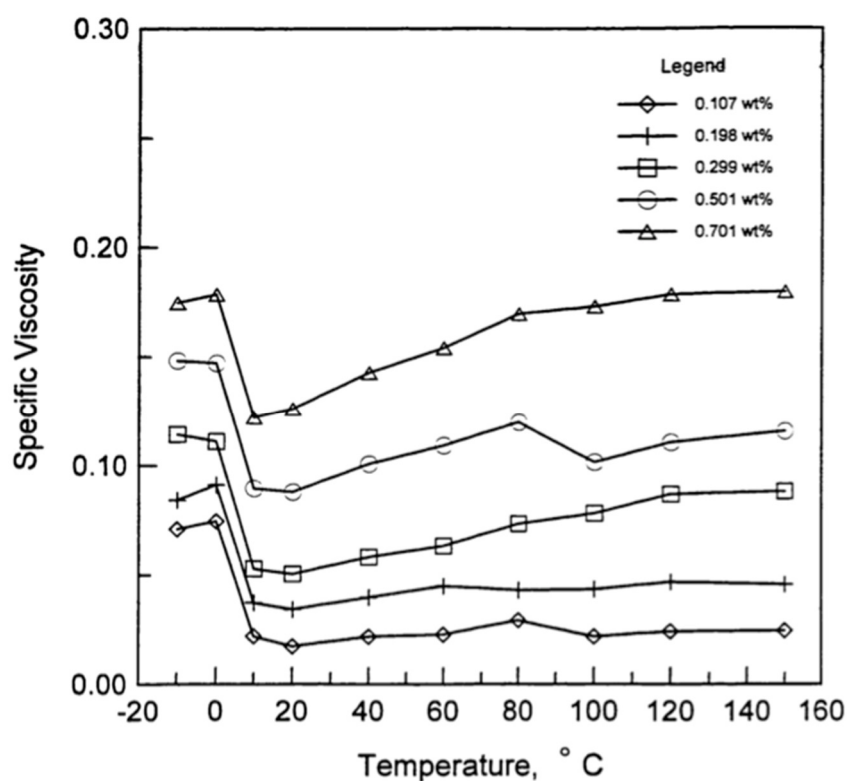


Fig. 2.11: Specific viscosity temperature dependency PMA [13]

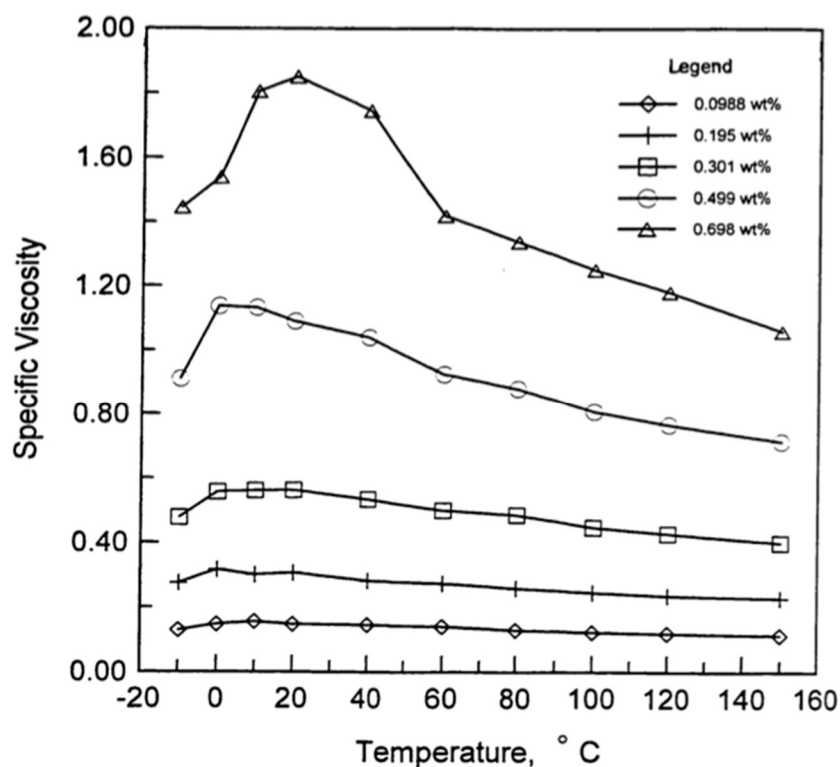


Fig. 2.12: Specific viscosity temperature dependency OCP [13]

2.5 VI-IMPROVING MECHANISM OF VISCOSITY MODIFIERS

There has been much debate as to the molecular mechanism by which VIIs increase the viscosity index of their blends. Selby [16] made the first major contribution. He proposed that as temperature is increased the polymer coil expands and consequently the hydrodynamic volume increases, as shown in figure 2.13. This leads to increased polymer overlap as well as the polymers influencing the flow of a larger number of base fluid molecules, both of which would promote an increase in viscosity. Selby's model also suggested that using solvents of better quality allows a polymer to expand further and so have more thickening power.

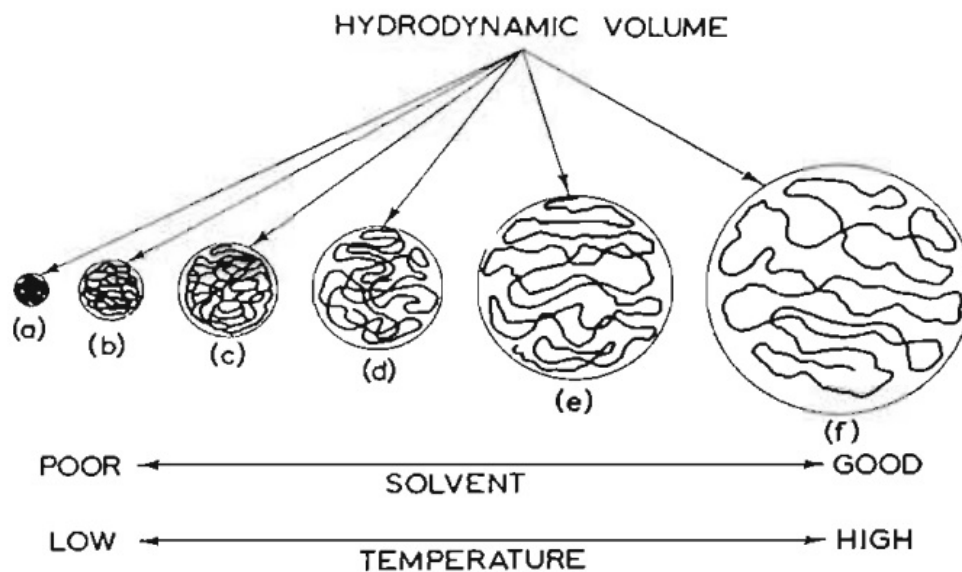


Fig. 2.13: VI mechanism: expansion and contraction of a macromolecule [12]

In the 1980s Mueller [12] challenged the mechanism proposed by Selby [16]. He noted that adding a polymer to a neat base oil actually increases the viscosity-temperature dependency when compared to the neat base oil. It is only when the polymer blend is compared to a different neat base oil having the same high viscosity at high temperature that the viscosity temperature-dependency is reduced over that of the polymer-free base oil. This implies that some of the increase in viscosity index originates from the way that VI is defined and varies with viscosity.

Experiments conducted on a Vogel-Ossag viscometer showed that whereas, for some polymer additives the coils indeed expand, for others they contract. Both types though lead to a viscosity index improvement when compared to a viscosity equivalent neat base oil. Mueller suggested that, while expanding coils may contribute to increasing the viscosity index, the expansion cannot be the sole source for improving the viscosity index [12].

Kulicke *et al* [17] found a linear viscosity increase with molecular weight for dilute polymer solutions. Depending on the quality of a solvent, the root-mean-square radius of gyration is either smaller or larger. For every solvent, the root-mean-square radius of a polymer follows a molecular weight related power law. When diluting polystyrene in cis- decalin, the relationship is:

$$\langle R_g^2 \rangle_w^{0.5} / nm = 0.023 M_w^{0.54} \quad (2.9)$$

Viscosity increases with polymer coil radius. Below a certain critical molecular weight, the viscosity increase appears independent of solvent.

Moore *et al* [18] found that more aromatic base oils improve the viscosity enhancing effect of VMs. Abou El Naga *et al* [19] confirmed this effect and related it to the swelling of the polymer.

Bezot *et al* [20] implemented a light scattering technique on styrene-hydrogenated butadiene. The authors found that as temperature and as solvent quality is increased, polymers are more and more distributed as isolated polymers rather than micelles of polymers.

In recent years there has been growing interest in the origins of VM behaviour, driven by techniques that enable polymer coil size to be measured in solution such as small angle neutron scattering [21] coupled with molecular dynamics simulation which can simulate polymer configuration in solution directly [22]. The molecular dynamics simulations confirm that PMAs increase in hydrodynamic volume when temperature is increased, whereas OCPs do not.

2.6 VISCOSITY INDEX IMPROVER EFFECT ON ENGINE PERFORMANCE

It is commonly recognised that less temperature-dependent oils (*i.e.* those with higher VI) may provide improved fuel economy by ensuring a lower viscosity at low temperature (and thus low friction) while still maintaining an acceptable viscosity at elevated temperature.

Swanson *et al* [23] tested several oils with and without VMs. Synthetic oils with higher VIs provided less oil heating due to less power losses when compared to low VI oils. A VM additive could be used in mild conditions in order to achieve an optimal oil.

Landry [24] showed that synthetic automatic transmission oils performed much better than mineral oils because it was possible to achieve a much lower low temperature viscosity without compromising on the high temperature viscosity. Recently Stohr *et al* have described the development of PMA-based polymers with long comb side-chains that are able to give very high VI blends and thereby high efficiency engine and transmission oils [25].

It should be noted, however that the above obvious benefit of high VI in contributing to low friction cannot be usefully considered without also taking account of the influence of shear thinning.

Kirschke [26] has stressed the importance of shear thinning properties of VMs and found that the impact of shear thinning on oil viscosity could outweigh the benefits in temperature dependency. The next chapter will outline the shear thinning behaviour of VII polymer solutions and the practical effects of this on hydrodynamic contacts.

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3 Viscosity modifiers: temporary shear thinning

This chapter reviews existing literature on the temporary shear thinning properties viscosity modifiers exhibit. Temporary shear thinning is believed to come primarily from the alignment of VMs in direction of shear. Shear stress is the dominant cause for shear thinning and not strain rate. VMs improve engine efficiency by shear thinning and also may improve surface protection. Too much shear thinning however may result in too thin oils and consequently in wear. High temperature high shear rate viscosity (HTHS) is introduced to provide a convenient measure of the extent of shear thinning of an engine oil.

3.1 INTRODUCTION

In 1953 Frazier *et al* [1] found that polymer-containing oils had the inexplicable ability to improve engine efficiency over straight base oils of same viscosity. Soon it would be understood that the viscosity of VM containing oils is shear dependent and that a shear dependent viscosity greatly impacts engine lubrication.

By the 1960s attention started to focus on understanding the mechanism and magnitude of the shear thinning behaviour of VM solutions. Selby [2] considered the molecular origins of polymer shear thinning and identified two processes. He explained the phenomenon of temporary shear thinning in terms of polymer molecules aligning along the shear direction, while permanent shear thinning occurs when the chains are stressed to the extent of fracturing permanently into shorter polymer chains. In the current work, the focus is on temporary shear thinning properties of VMs, so permanent shear thinning, although important to engine lubrication, will not be reviewed or discussed in any detail in this thesis.

Selby [2] also found experimentally that the viscosity due to severe temporary shear thinning tended towards the base oil viscosity. Thus all of the viscosity-enhancing ability of a VM in solution may be lost in harsh conditions.

At about the same time, Horowitz [3,4] obtained experimental data underlying the concept that temporary shear thinning is a function of shear stress. He made the first attempt to fit an empirical law with his experimental data [3] and applied his law in a journal bearing model [4]. Horowitz found that the eccentricity ratio increased and thus film thickness decreased when utilising a polymer-containing oil compared to a straight mineral oil of same low shear rate viscosity.

In the 1960s and 1970s concern grew about the impact of shear thinning on engine bearing durability as it was realised that shear thinning would lead to a reduction in hydrodynamic film thickness. This led to the need to include in engine oil classifications a measure of viscosity at typical engine bearing conditions. After extended debate, by 1983 a lower limit value of viscosity at 10^6 s^{-1} and 150°C was included in European engine oil specifications – although it was not until 1990 that a similar requirement was included in US specification GF-1. There was also great interest in the late 1970s and 1980s to improve engine efficiency and a growing awareness of the fact that shear thinning could reduce engine friction and thus be a route to fuel-efficient engine oils. This led in 1995 to the inclusion of a fuel economy engine test in GF-2 and the development in Europe of the CEC M111 engine test to measure fuel economy in 1996.

Since the 1990s increasing concern to reduce energy consumption in vehicles has led to progressively more demanding fuel economy engine tests in engine oil specifications and the temporary shear thinning behaviour of VM-containing oils is now recognised to be a valuable resource in the design of low friction lubricants.

3.2 MECHANISM OF SHEAR THINNING

Selby illustrated his proposed mechanisms of temporary and permanent shear thinning as shown in figure 3.1, with temporary shear thinning resulting from partial polymer alignment and permanent shear thinning from polymer scission [5].

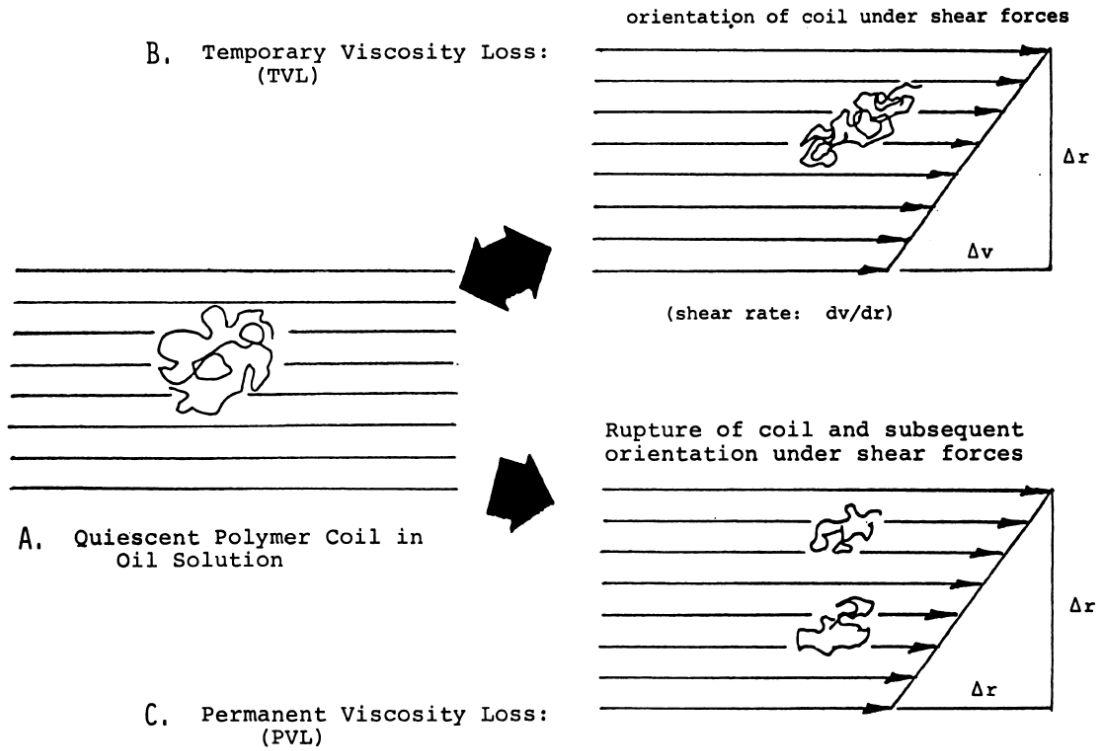


Fig. 3.1: The difference between temporary and permanent shear thinning [5]

In 1991 Cann and Spikes [6] applied an innovative infrared (IR) spectroscopy technique to a ball on an IR transparent disc lubricated contact to determine the IR absorption ratio of polymer, $\frac{A_{\text{polymer C=O}}}{A_{\text{base oil C-H}}}$, at different speeds, where $A_{\text{polymer C=O}}$ is the IR absorbance at the carbonyl bond stretch wavelength while $A_{\text{base oil C-H}}$ is that of the hydrocarbon bond. When the IR radiation was polarised in the direction of entrainment, the ratio increased, while when it was polarised in the in-plane normal direction to entrainment, the ratio remained constant. This indicated that the VM molecules were aligned in direction of shear. Furthermore, as speed was increased, the ratio increased further, indicating an increased alignment of the polymer with applied shear rate. The

authors correlated the alignment indicated by absorbance ratio with shear dependent viscosity measurements, as shown in figure 3.2.

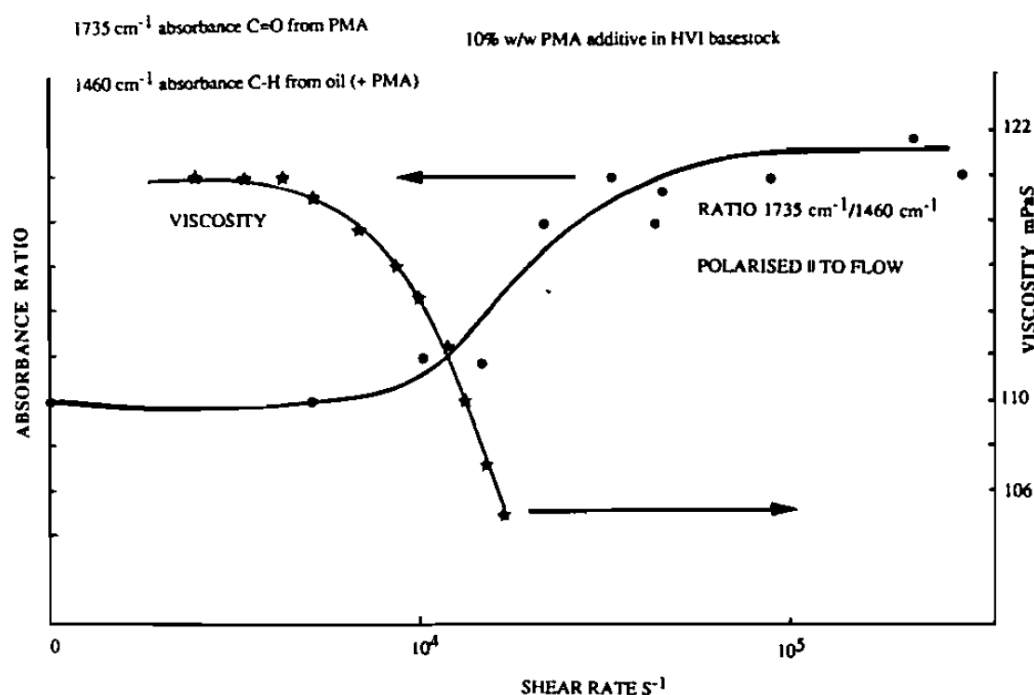


Fig. 3.2: Polymer elongation vs viscosity correlation, summary of shear rate results for polarised VI spectra [6]

Selby's concept of the temporary shear thinning mechanism was further supported by Lee and Muller who visualised polymer molecular alignment using a light-scattering technique [7,8]. The technique was applied to polystyrene in phthalate ester solutions and showed that polymers increasingly aligned in the direction of shear as solvent quality was reduced, as shown in figures 3.3 and 3.4. These findings are in contrast to Zisenis and Springer [9-12] who conducted the same experiments on lower viscosity oils and concluded the opposite behaviour when varying solvent quality.

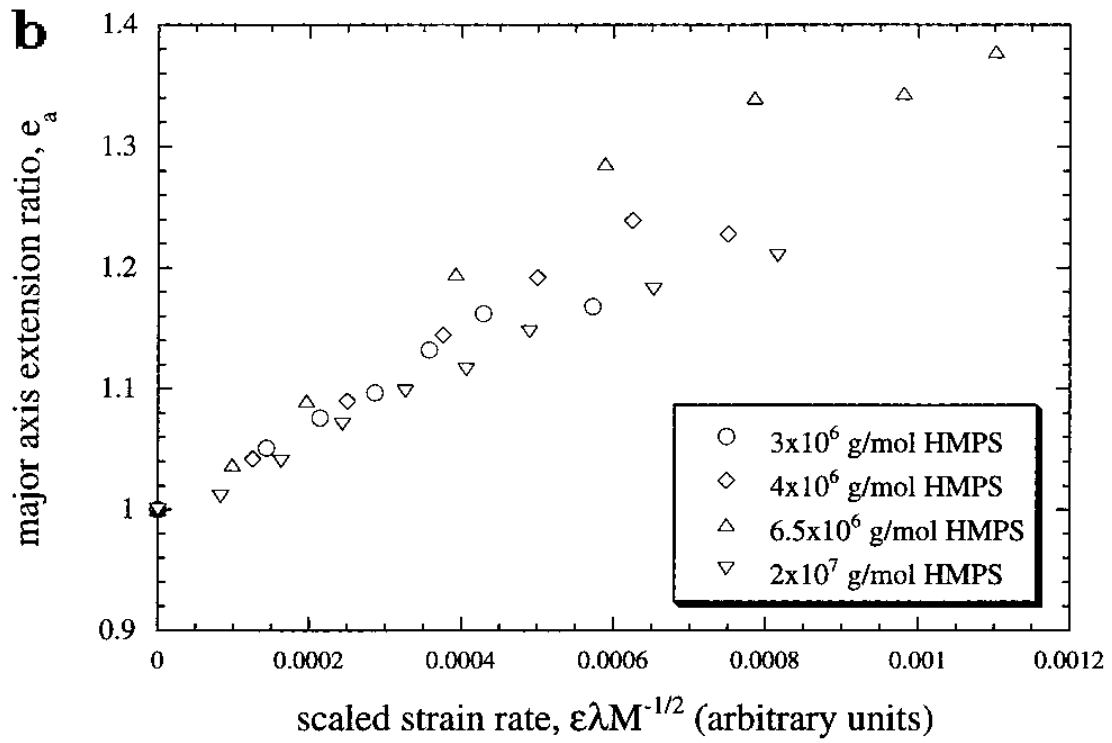
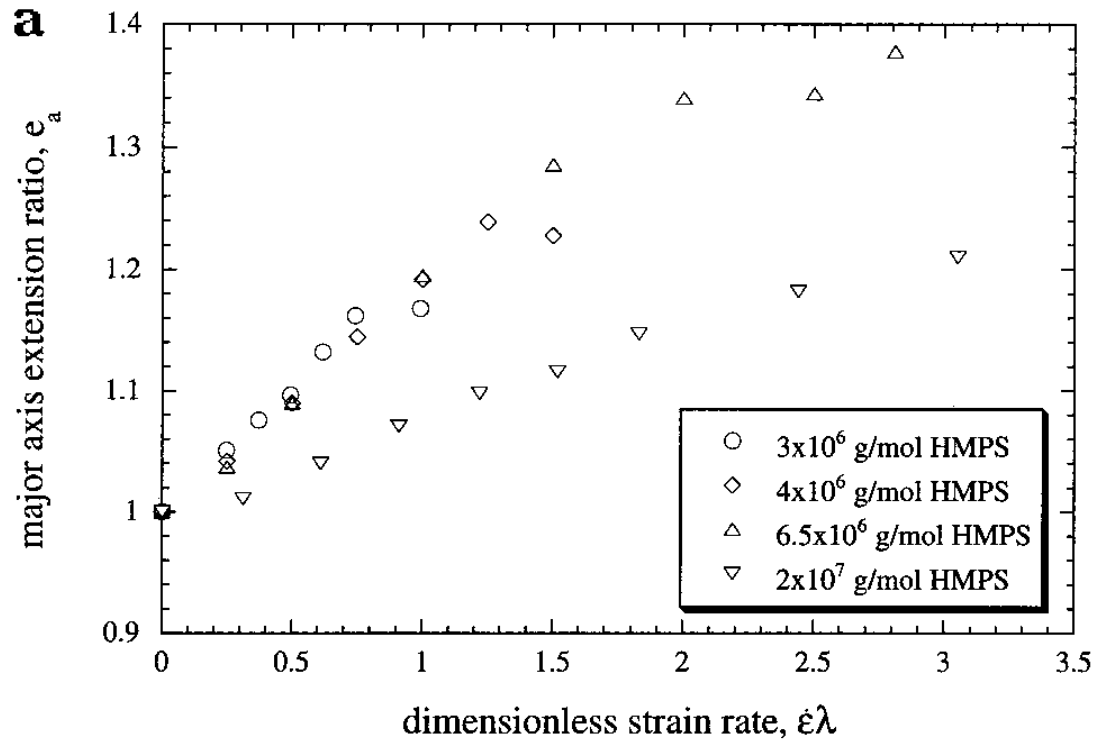


Fig. 3.3: Major axis extension ratio due to shear thinning at 13°C [8]

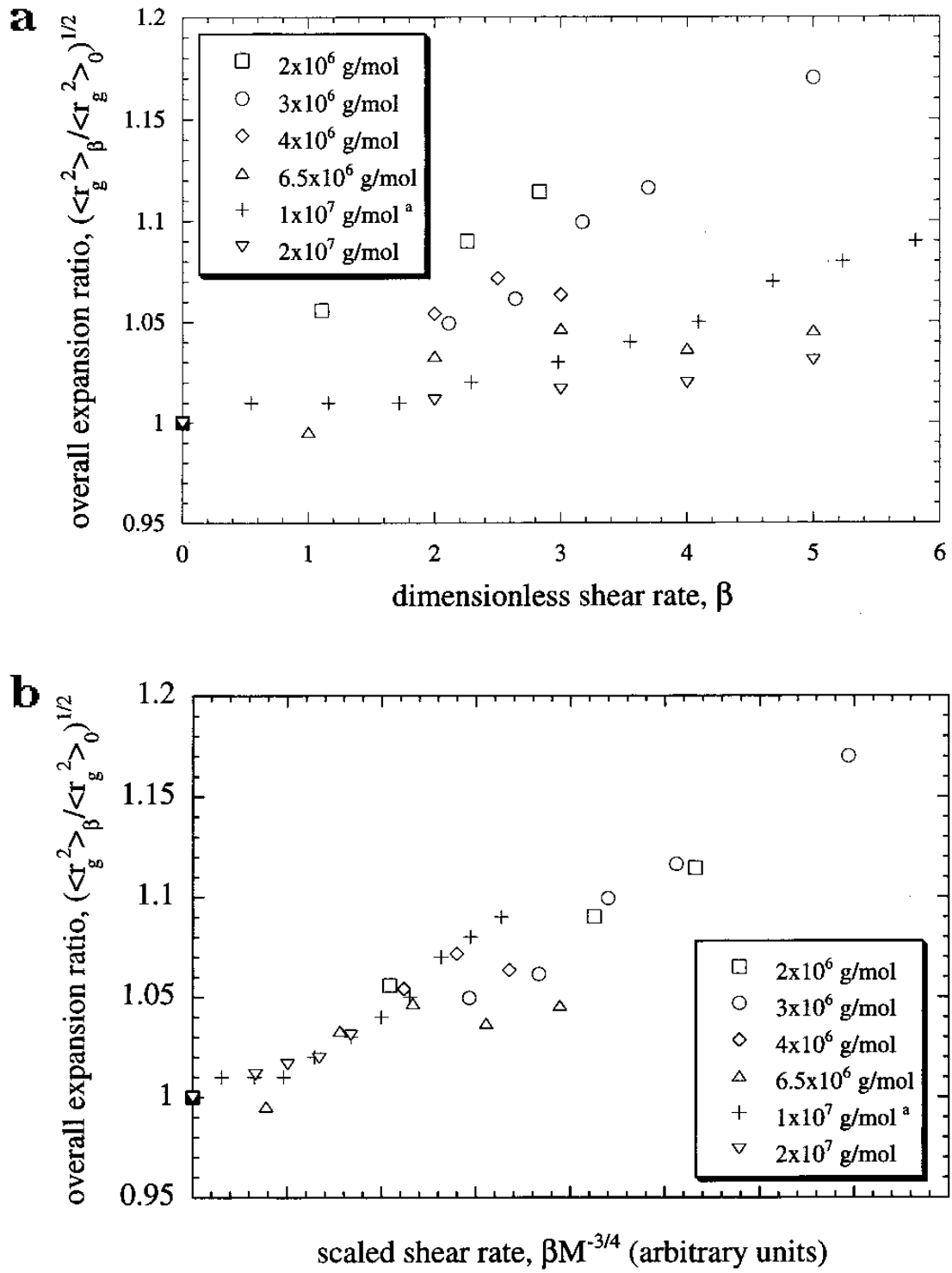


Fig. 3.4: Overall VM expansion ratio due to shear thinning at 25°C [8]

3.3 SHEAR THINNING EQUATIONS

In the 1960s and 1970s Cross (Eq. 3.1) [13] and Carreau (Eq. 3.2) [14] developed equations to describe the dependence of viscosity on strain rate for polymer solutions. Carreau's equation was subsequently modified by Yasuda based on experimental measurements on polymer solutions to give the equation now known as the Carreau-Yasuda equation (Eq. 3.3) [15].

Cross equation:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + p\dot{\gamma}^q} \quad (3.1)$$

Carreau equation:

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})(1 + (\lambda\dot{\gamma})^2)^{(n-1)/2} \quad (3.2)$$

Carreau-Yasuda equation:

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty})(1 + (\lambda\dot{\gamma})^a)^{\frac{n-1}{a}} \quad (3.3)$$

Wright *et al* [16] tested the fit to experimental data of the Cross equation and also two other shear thinning equations, by Lyons (Eq. 3.4) and Badiali (Eq. 3.5). Furthermore, they developed and tested versions of these equations in which shear stress was allowed to vary with temperature (Eq. 3.6-8). All of these equations gave good fit to experimental data but the authors expressed a slight preference to the Cross equation and recommended users to avoid predicting viscosity outside of the measurable shear rate range.

Sorab *et al* [17] successfully matched experimental shear thinning data to the Carreau equation.

Lyons' equation:

$$\frac{\eta}{\eta_0} = \frac{1 + d\tau}{1 + c\tau} \quad (3.4)$$

Badiali's equation:

$$\eta = \frac{j(1-\exp(-i\dot{\gamma}))}{\dot{\gamma}} + k \quad (3.5)$$

Lyons' temperature dependent equation:

$$\frac{\eta}{\eta_0} = \frac{1+f\tau \times \exp\left(\frac{h}{T}\right)}{1+g\tau \times \exp\left(\frac{h}{T}\right)} \quad (3.6)$$

Badiali's temperature dependent equation:

$$\frac{\eta}{\eta_0} = \frac{\eta_\infty}{\eta_0} + \frac{\left(1-\frac{\eta_\infty}{\eta_0}\right)\left(1-\exp\left(-l\dot{\gamma}\exp\left(\frac{m}{T}\right)\right)\right)}{l\dot{\gamma}\exp\left(\frac{m}{T}\right)} \quad (3.7)$$

Cross' temperature dependent equation:

$$\frac{\eta}{\eta_0} = \frac{\eta_\infty}{\eta_0} + \frac{1-\eta_\infty/\eta_0}{1+\text{antilog}\left(u+q\log(\dot{\gamma})+\frac{s}{T}\right)} \quad (3.8)$$

3.4 INFLUENCE OF SHEAR STRESS

Despite the fact that the above temporary shear thinning equations are expressed in terms of strain rate, many studies have suggested that the key driver is actually shear stress. The earliest was by Horowitz [3] who showed that shear thinning measured at various temperatures collapsed on a single curve when plotted against shear stress, i.e. the product of strain rate and measured viscosity.

In 1983 Hamilton *et al* [18] investigated shear thinning in concentric cylinders under high pressure and concluded that temporary shear thinning was solely dependent on shear stress.

Hutton *et al* [19] measured shear thinning of polystyrene at different pressures and plotted the results against the product of strain rate and viscosity corrected for the effects of temperature and pressure as shown in figure 3.5:

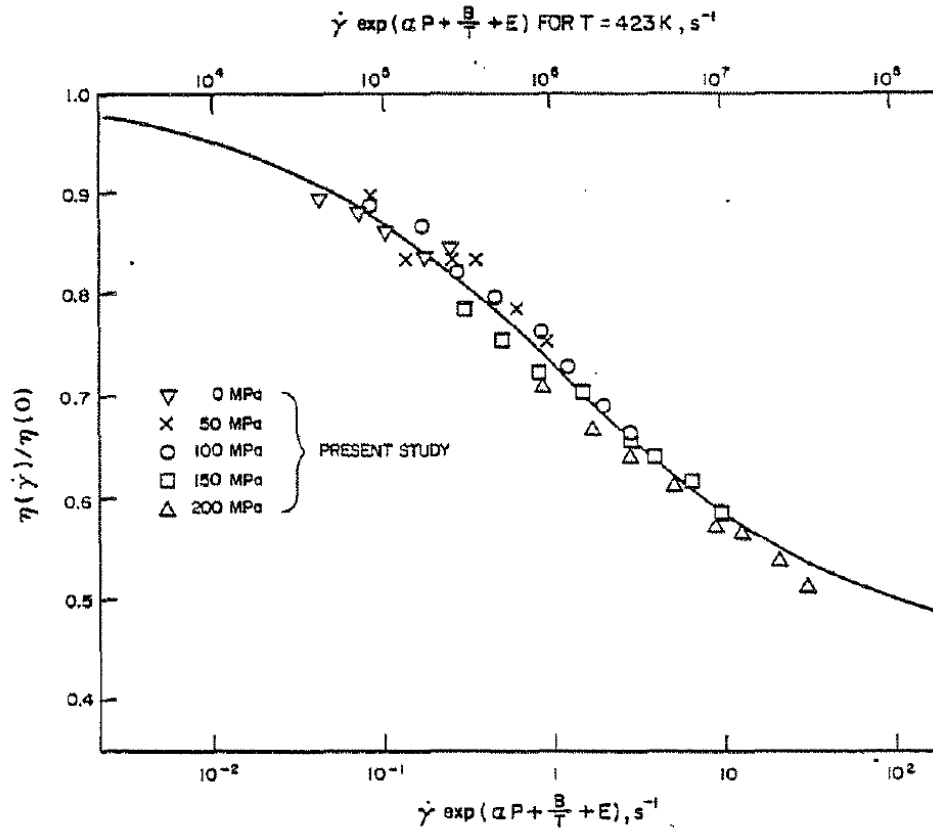


Fig. 3.5: Shear thinning of polystyrene for different pressures [19]

This product is of course the shear stress and the authors found that plotted in this way all of the shear thinning data fell on one master curve.

More recently Chen *et al* [20] also showed that the extent of shear thinning of several polymers collapsed when plotted against shear stress to form one master curve regardless of concentration and temperature. This remained valid below a certain limiting shear stress and as long as the concentration is low enough that polymer-to-polymer interactions were negligible so that shear thinning solely depended on polymer-base-oil interaction.

Bezot *et al* [21] showed the temperature and shear rate dependency of styrene-hydrogenated butadiene (figure 3.6). As temperature or shear rate was reduced, the amount of shear thinning was reduced, again consistent with shear thinning being directly influenced by shear stress.

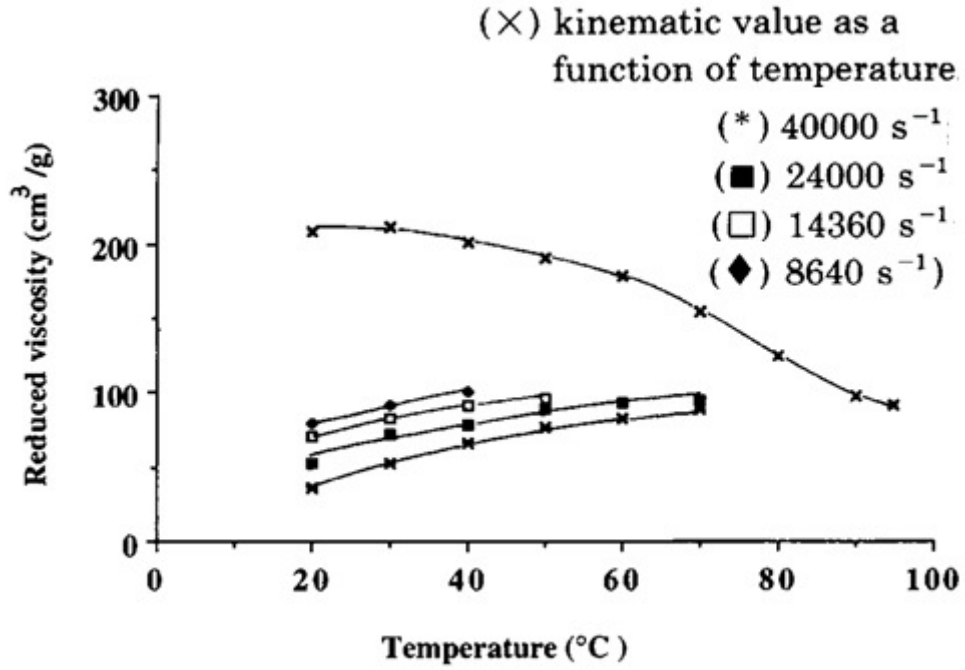


Fig. 3.6: Temperature and shear rate dependence of the reduced viscosity of a 2.5% wt blended SHB copolymer [21]

3.5 SHEAR STABILITY INDEX

Various measures have been used to quantify the extent of shear thinning under any conditions. Horowitz [3] used specific viscosity, η_s , i.e.

$$\eta_{sp} = \frac{\eta - \eta_{base}}{\eta_{base}} \quad (3.9)$$

where η is the solute viscosity and η_b the base oil viscosity, since this value is relatively insensitive to polymer concentration. He then described shear thinning as the reduced viscosity, i.e. the ratio of specific viscosity at high shear stress to the specific viscosity at low shear, as shown in figure 3.7.

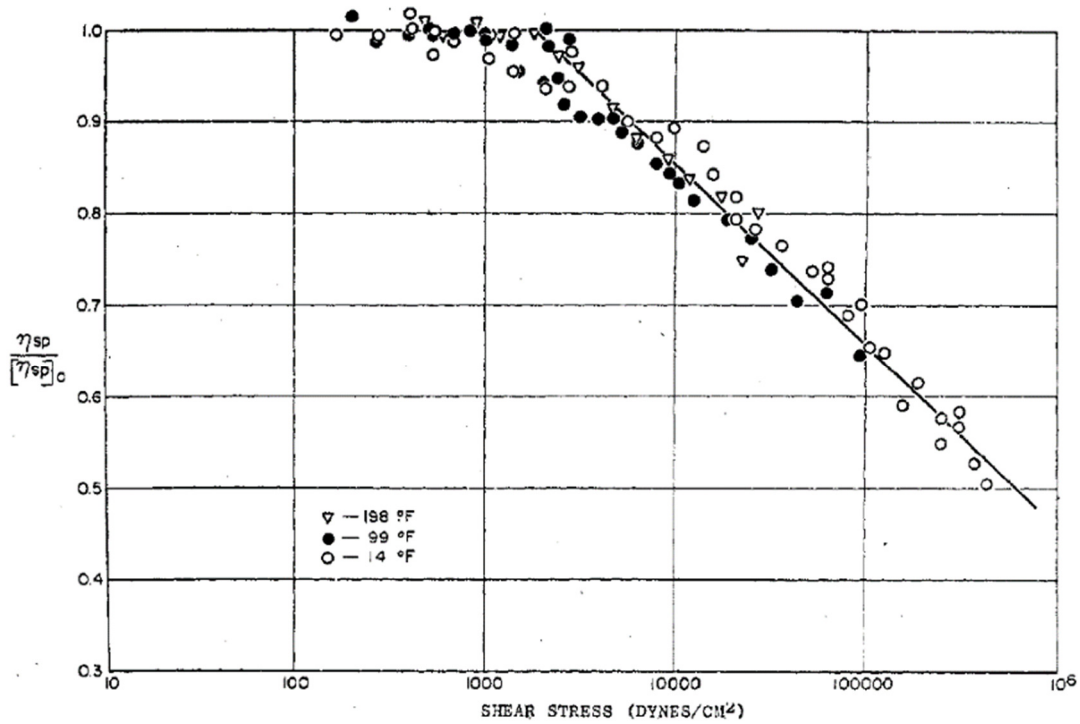


Fig. 3.7: Reduced specific shear thinning viscosity against shear stress for different temperatures [3]

More recently Dobson [22] showed experimentally that the temporary shear thinning shear stability index (SSI) as defined by Eq. 3.10 provided a useful means of comparing effectiveness of different VMs. Moreover, one single SSI curve is sufficient to infer the effect of VM concentration in the blend. Hence, SSI was a better comparison value than reduced viscosity. Some of his results are shown in figure 3.8.

$$SSI = \frac{\nu - \nu_{\infty}}{\nu_0 - \nu_{\infty}} \quad (3.10)$$

The SSI corresponds to the loss in viscosity thickening power of a polymer compared to its viscosity contribution to the base oil at zero shear. It may be expressed by either dynamic or kinematic viscosity since density will not change significantly due to shear; in figure 3.8 Dobson used kinematic viscosity.

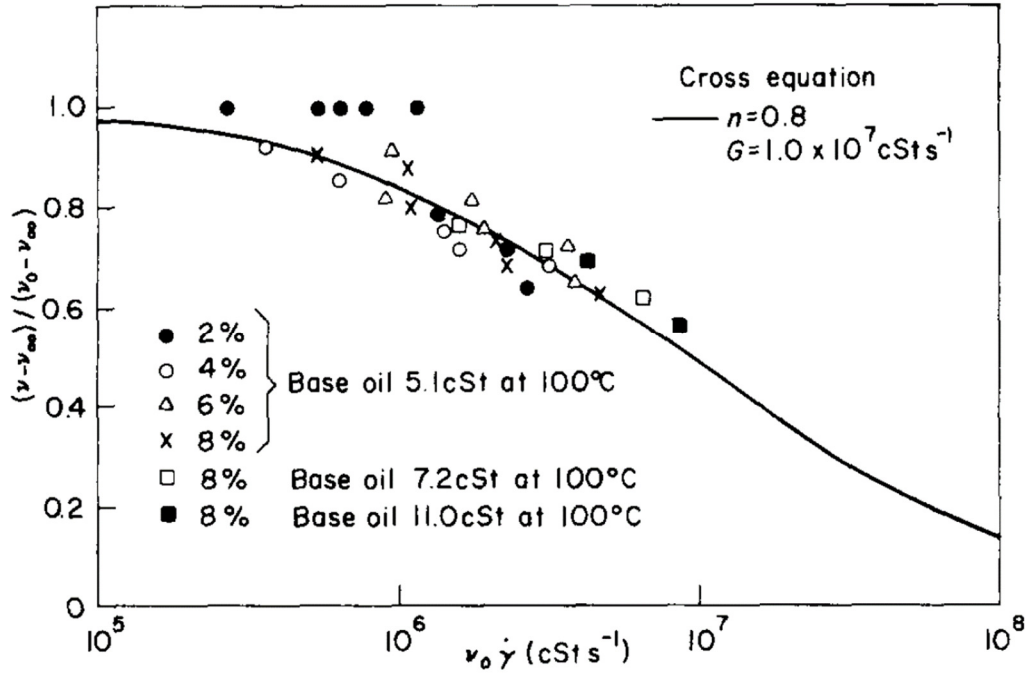


Fig. 3.8: Effect of concentration on the SSI vs shear stress [22]

The SSI actually comes directly from most of the shear thinning expressions in section 4.3. Thus rearrangement of the Cross equation, Eq. 3.8, gives;

$$SSI = \frac{1}{1+p\dot{\gamma}^q} \quad (3.11)$$

while Badiali's temperature-dependent Eq. 3.7 reduces to;

$$SSI = \frac{1 - \exp(-l\dot{\gamma}e^{m/T})}{l\dot{\gamma}e^{m/T}} \quad (3.12)$$

It was found that different polymer types shear thin by different amounts and George and Hedrick [23] obtain experimental flow curves of different VM concentrates against shear stress and studied the dependence of shear thinning on temperature. Radial hydrogenated isoprene appeared almost Newtonian over the test conditions applied while dispersant styrene esters and polymethacrylate showed slight shear thinning.

Olefin copolymers showed gradual shear thinning and styrene-hydrogenated butadiene exhibited a significant amount of shear thinning.

Stambaugh [24] related the percentage of molecular weight in the backbone of a polymer to the amount required in order to obtain a same low shear viscosity thickening power. Figure 3.9 illustrates the correlation between backbone molecular weight percentage and concentration required to provide a set SSI for different VM polymers.

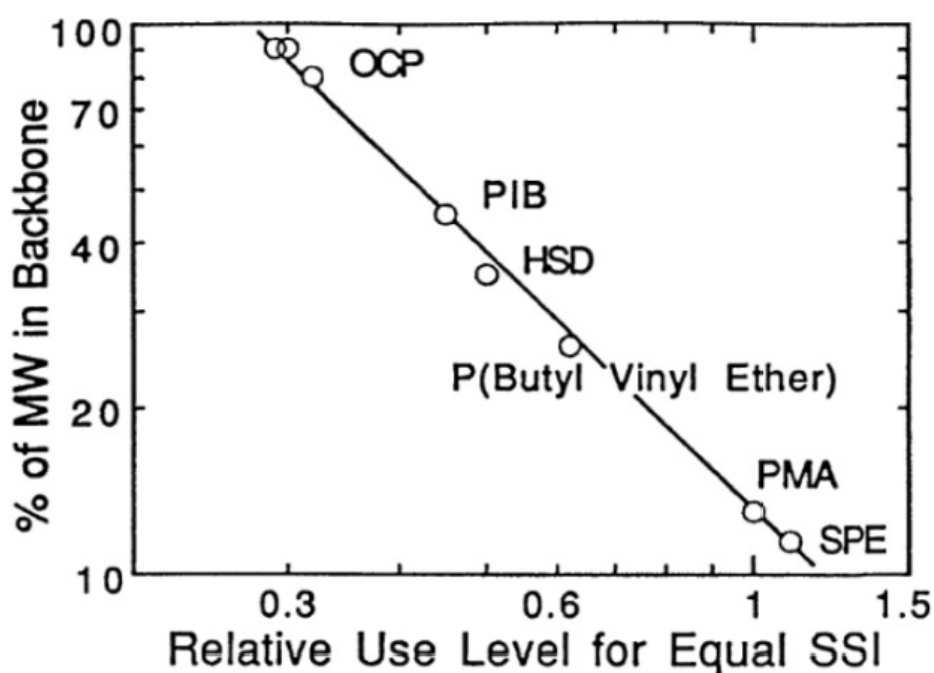


Fig. 3.9: Relative thickening efficiencies of various VI improvers [24]

Thus for primarily linear VMs such as OCPs, where most of the molecular weight is in the backbone, less polymer is needed to give a set SSI than when the polymer has substantial side chains, as with PMAs. Polymers with side chains shear thin less at a given concentration, so higher concentrations are needed to give the same SSI.

3.6 HTHS

By the mid 1970s concern was growing about the impact of temporary shear thinning of engine oils on bearing film thickness and thus engine wear and failure. It was realised that revised engine oil viscosity classifications were needed that included measurements of the shear stability [25]. Sub-committees of both ASTM and CEC were established to study this and after a series of reports and studies this led eventually to the acceptance of the conditions 10^6 s^{-1} shear rate and 150°C as being representative of engine bearings. Thus the “High Temperature High Shear” (HTHS) viscosity measured at these conditions was taken to be appropriate to assess likely performance in engines [26,27]. Viscometers were developed to measure lubricant viscosity under these conditions and once this was done HTHS thresholds were included as a requirement in the SAE J300 engine oil classification. There are currently two standard methods of measuring HTHS implementing either a tapered-plug viscometer [28] or a multicell capillary viscometer [29]. Although the initial motivation for developing a measure of HTHS was to ensure adequate film thickness and thus prevent wear, the importance of HTHS in terms of engine friction was soon recognised, as illustrated in figure 3.10 [26].

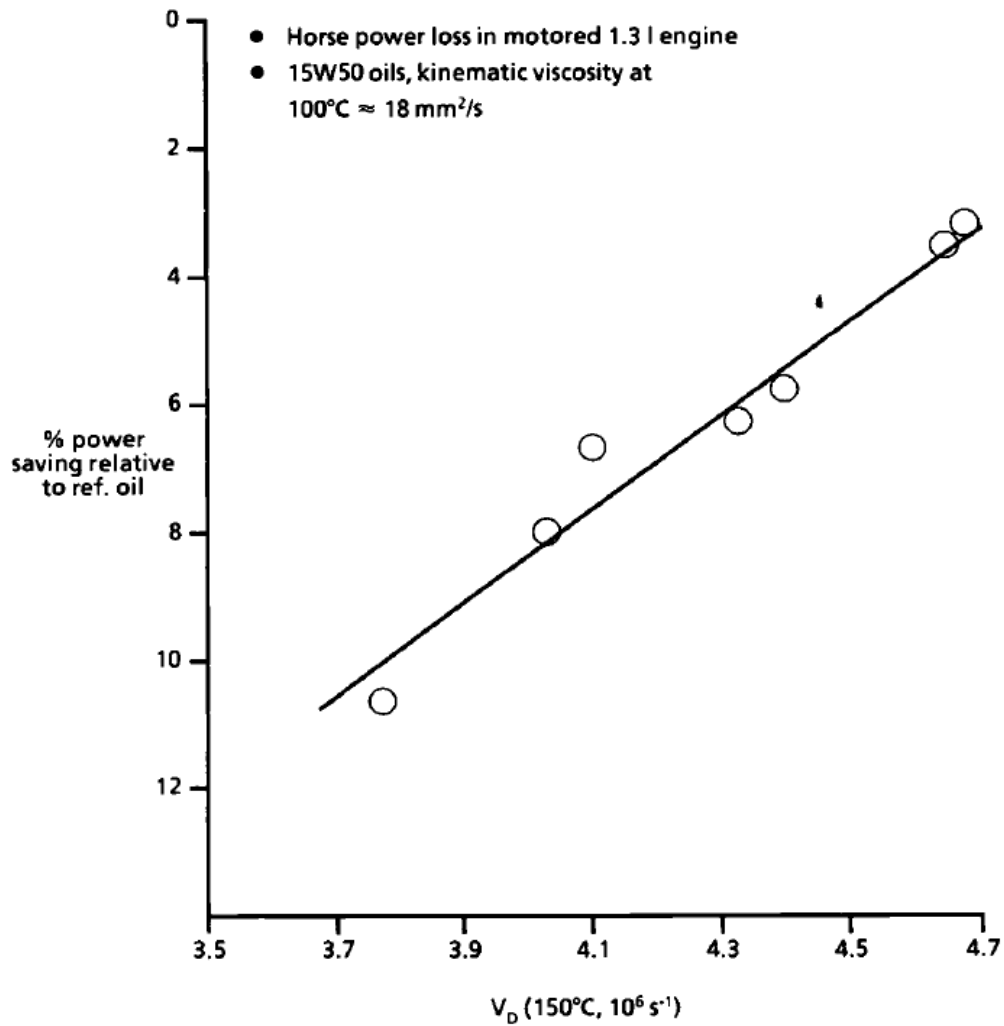


Fig. 3.10: Dependency of engine friction on HTHS [26]

3.7 INFLUENCE OF SHEAR THINNING ON FILM THICKNESS

Since viscosity of VM-containing oils is shear stress dependent and film thickness is viscosity dependent, it is evident that shear thinning is likely to reduce film thickness, as indeed was the concern with respect to engine bearing performance that led to the development of HTHS. Two different conditions have been researched experimentally: non-conforming, high-pressure contacts and conforming, low-pressure contacts.

3.7.1 HIGH PRESSURE EHL CONTACTS

Ever since the development of optical interferometry to study EHD film thickness this method has been used to explore the impact of shear thinning on the EHD film thickness of polymer solutions. In 1968 Foord *et al.* [30] showed that VM-containing blends gave thinner film thicknesses than expected based on EHD theory and suggested that this originated from shear thinning in the inlet. Using an expression for shear thinning rate due to Dyson they estimated the temporary viscosity loss.

Yoshida *et al* [31] tested a range of polymethacrylate VMs with MWts between 40k and 900k g/Mol in order to investigate the impact of polymer molecular weight variation on film thickness. Film thickness was always considerably thinner for polymer-containing oils than for Newtonian oils of same low shear rate viscosity. Furthermore, for a same low shear viscosity, increasing the molecular weight led to decreasing film thickness until it matched that of the base oil. The authors also used sonic treatment to permanently degrade the lubricant and reduce the average molecular weight of the solution. Surprisingly this led to an increase in EHD film thickness. Yoshida *et al* ascribed this to smaller polymer molecules entering the contact more easily than larger, intact molecules. An alternative explanation is that the lower molecular weight molecules formed by degradation had less tendency to temporarily shear thin in the inlet and this outweighed the thickening due to higher MWt.

Bair and Winer found good correlation between EHD interferometric film thickness measurements and values calculated from Hamrock and Dowson's EHD theory for Newtonian oils [32]. For VM containing oils, however, thinner films were measured than those predicted from low shear rate viscosity. Using measured pressure-viscosity data they compared theoretical film thicknesses with experimental ones to obtain effective inlet viscosities of the polymer solutions. Bair and Hamrock also measured EHD friction and found the measured values for polymer solutions to be much less than those from equivalent low shear rate viscosity base oils.

Moore *et al* [33] tested the film thickness of styrene-butadiene VM solutions in PAO base oils at inlet conditions comparable to a representative engine shear rate of 10^7 s^{-1} .

The authors concluded that under these severe conditions in a ball on disc setup, the film thicknesses were as low as those of the base oil. Film thickness measurements on two disc rollers [34] and on a camshaft laboratory test rig [35] showed that for other test geometries also, the addition of a VM hardly improved film thickness over that of a base oil in full film lubrication.

The effect of varying concentration of VM on shear thinning was monitored by Cooper and Moore using optical interferometry [36]. At low concentrations of VMs in oils, the effective viscosity inferred from the film thickness was that of the base oil. However for high concentrations of VM, the effective viscosity was greater than the base oil.

Like Yoshida [31], Mitsui *et al* [37] found an increasing reduction of film thickness compared to the value predicted from low shear viscosity as molecular weight was increased. For very low molecular weights, no shear thinning effect on film thickness was observed. For higher molecular weights measured film thickness could be determined from the solution's viscosity based on intrinsic viscosity.

Wardle *et al* [38] defined and implemented polymer efficiency PE as shown in Eq. 3.13-15 in order to compare the influence of molecular weight and type of VM. Here h_c is the central film thickness and η the dynamic viscosity.

$$PE = \frac{\text{experimental } \Delta h_c}{\text{predicted } \Delta h_c} \quad (3.13)$$

$$\text{experimental } \Delta h_c = \frac{h_c(\text{blend}) - h_c(\text{base oil})}{h_c(\text{base oil})} \quad (3.14)$$

$$\text{predicted } \Delta h_c = \frac{\eta(\text{blend})^{0.67} - \eta_{\text{base}}^{0.67}}{\eta_{\text{base}}^{0.67}} \quad (3.15)$$

From experimental EHD tests it appeared that polymer efficiency decreased linearly with molecular weight regardless of polymer type or concentration of the blend.

Oestensen [39] used a viscometer to obtain high shear stress viscosities of VM-containing oils. He then correlated high pressure EHD ball on disc film thickness measurements with Hamrock and Dowson's predictions using the shear thinned viscosity at the mean contact shear stress. Figure 3.11 illustrates the correlation.

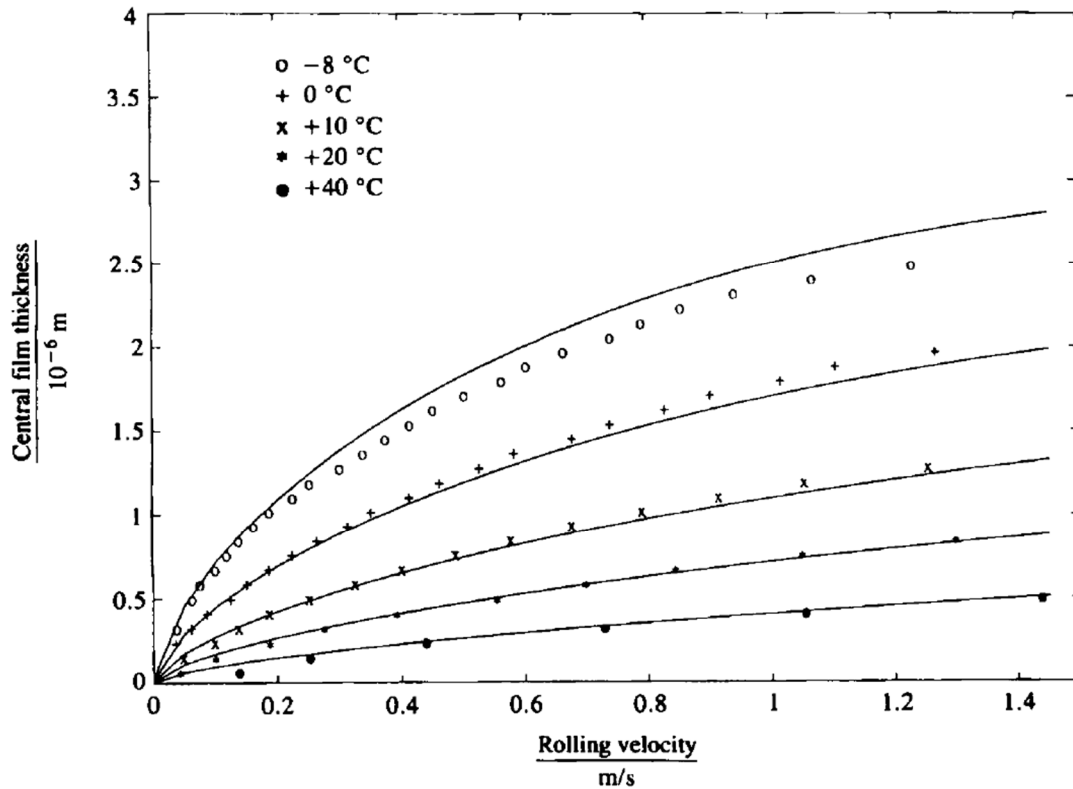


Fig. 3.11: Theoretical predictions and experimental central film thickness of a shear thinning oil at different temperatures [39]

In interpreting and understanding the effect on polymer shear thinning on EHD film thickness it is important to recognise that EHD film thickness is primarily determined by the viscosity of the lubricant in the immediate contact inlet; its viscosity in the central region of the contact has little effect. For shear thinning oils, viscosity will vary across the inlet in response to both pressure and shear rate. The volume of lubricant entrained and thus the film thickness will then depend on a complex average of the viscosity over the inlet region.

One approach to this problem is to use representative values for inlet pressure and shear rate across the inlet to evaluate a representative inlet viscosity from which to calculate

film thickness. Dyson [40] has shown that the maximum shear rate in the inlet in pure rolling is $3U/2h$, where U is the entrainment speed and h the central film thickness and has also shown how this varies with slide roll ratio. Furthermore, it has been suggested that a representative inlet pressure is 80 MPa [41]. For fluids with a pressure viscosity coefficient of $\alpha = 15 \text{ GPa}^{-1}$ and assuming viscosity to be related to pressure by Eq. 3.16

$$\eta = \eta_0 e^{\alpha \bar{P}} \quad (3.16)$$

the latter would suggest an increase in viscosity (and thus the shear stress) from the atmospheric pressure value in the inlet region of about a factor of three.

A second approach is to solve the Reynolds equation component of the EHD problem assuming a Grubin-type film geometry, thus allowing the extent of shear thinning of the lubricant to vary across the inlet. This was first done by Dyson and Wilson for a power law shear thinning fluid [40] and a similar approach was used by Bair and Khonsari [42]. It is also, of course possible to carry out a full EHD analysis based on non-Newtonian fluid behaviour [43].

3.7.2 LOW PRESSURE CONTACTS

It is more difficult experimentally to set up a conforming, low-pressure hydrodynamic contact than a non-conforming high pressure one due to problems of precise alignment of near parallel surfaces and the high loads required. This will be further discussed in Chapter 4. This means that experimental measurements of hydrodynamic film thickness have tended to be made in real engine components such as plain bearings and piston assemblies.

There has been considerable research on oil film thickness in engine journal bearings. This has mostly been based on measurement of the total electrical resistance or capacitance of operating bearings, with minimum film thickness calculated from an assumed circular bearing shape [44].

More recently it has been shown that ultrasonic transducers can be used to measure journal bearing film thickness, but the application of this has so far been limited [45].

Since the 1970s, many researchers have studied the influence lubricant rheology and bearing film thickness and all have observed that for VI-improved oils, minimum oil film thickness correlates better with viscosity measured at high shear rate than that measured in conventional low shear viscometers [27,46,47]. However this correlation appears not to be straightforward. Deysakar noted that, while viscosity predicts film thickness very well for monograde oils, the correlation with HTHS for multigrade oils is less reliable and deviations from good correlation appears to be VM-type specific [48]. Various possible reasons for this were suggested including possible fluid elastic response and permanent viscosity loss. More recently Tseregounis *et al* have reported a similar finding and tentatively ascribed it to polymer degradation [49].

Compared to engine bearings there has been far less experimental work to study the impact of shear thinning on film thickness in pistons. This is despite the fact that methods of measuring piston ring film thickness are well developed. These have been reviewed by Sherrington and Smith [50] although the more recent ultrasonic approach [51] should be added to the techniques described.

Hoult *et al* [52] measured film thicknesses in the piston assembly using laser induced fluorescence and found that multigrade oils gave less oil in the inlet region than monogrades, an effect they ascribed to different wetting properties. Arcoumanis and Ostova [53] both measured and modelled piston lubrication. They found that measured film thickness was equal to or smaller than the predicted film thickness obtained from low shear viscosity, but greater or equal to film thickness predicted from HTHS measurements. Their shear rates were quite high and they suggested viscoelasticity of the lubricant as possible reason for a film thicker than predicted from HTHS.

3.8 SHEAR THINNING AND WEAR

In general bearing wear would be expected to depend on minimum oil film thickness and thus depend similarly on polymer shear thinning, at least in the absence of polymer boundary film-forming behaviour.

Okrent [54,55] found in engine tests that polymer-containing oils decreased friction compared to Newtonian mineral oils of the same viscosity at a given temperature (an equivalent Newtonian mineral oil) [54]. To his surprise, they also decreased wear, even though they produced lower film thicknesses than the equivalent mineral oils [54]. Furthermore, it appeared that the wear reduction was dependent on molecular weight, blend concentration and polymer type. Later on Okrent concluded, by utilising metallic surface adsorbing detergents, that the tested VMs must also adsorb onto the metallic surface and thus decrease wear [55].

Selby researched the temperature effect of VMs and successfully correlated HTHS viscosity to journal bearing wear. He summed up research on lubrication to the end of the 1980s as: “It seems obvious that we still have much to learn about the lubricating process even at such an apparently simple level as viscosity.”

In contrast to Selby’s [56] findings, Hutton *et al* [19] suggested that HTHS values measured at atmospheric pressure might not correlate to bearing wear due to pressure effects on shear thinning.

In 1992, Demmin *et al* [57] conducted a detailed study of the correlation between HTHS and wear in engines by running nine oils in 45 taxicabs in New York and also using a chassis dynamometer test. Wear was measured from the taxicab engines. It was found that non-Newtonian oils provided slightly improved protection. For an HTHS above 2.6cP no significant wear in the thrust bearings was observed for up to 100,000 miles. For an HTHS of 2.45cP connector rod and main bearings were still sufficiently protected, while an HTHS of 2.1cP gave significant bearing wear. Finally, a limiting viscosity of 2.3-3.6cP was identified, below which undesirable effects may occur [19, 58-61].

3.9 THICK BOUNDARY FILM FORMATION

In the context of film thickness and wear, it should also be noted that since the 1990s it has been known that some polymers, especially functionalised ones with dispersant capability, can form adsorbed boundary films up to 20 to 40 nm thick and comparable to the undeformed polymer coil diameter in solutions. While such film thicknesses are much less than the minimum oil film thicknesses generally measured in journal bearings they may still be significant in reducing wear.

In 1994 Cann and Spikes [6] detected an “immobile film” of 17 nm thickness in a lubricated EHD contact in slow entrainment speed conditions. At higher entrainment speeds this was augmented by a hydrodynamic film. The authors hypothesised that the thickness of the immobile film corresponded to the size of two polymer coils of the polymer in the solution. This would then mean that a monolayer of polymer was adsorbed to each rubbing surface.

This early work used model polymers but in the mid-1990s Smeeth *et al* [62] compared the behaviour of solutions of a range of commercial VMs and found that some were able to form thick boundary films while others did not. Boundary film forming behaviour occurred only with PMAs and dispersant-functionalised copolymers (figure 3.12).

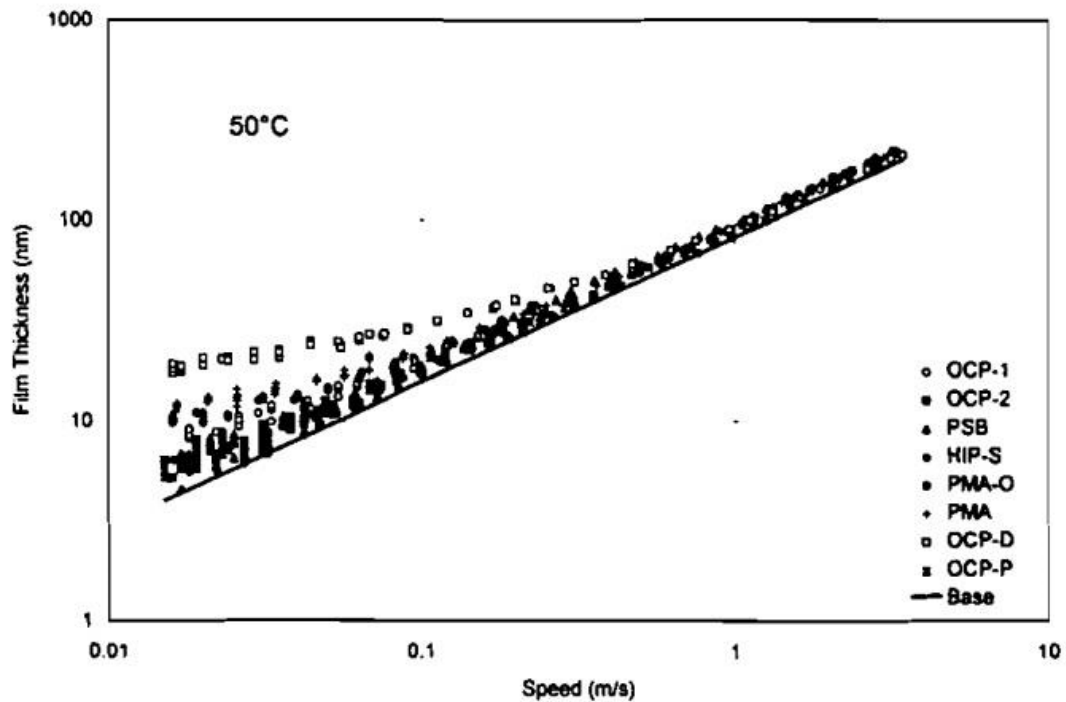


Fig. 3.12: Mixed and boundary film at 50°C formed by VMs blended at 6% wt. [62]

Gunsel *et al* [63] showed that those polymers that formed thick boundary films also reduced friction and wear in low speed boundary lubrication conditions.

Recently Fan *et al* [64-66] have studied the boundary film forming and consequent friction and wear behaviour of functionalised PAMA VMs. A series of well-defined polymers with different functionalities, polymer architectures and molecular weights were synthesised. It was found that copolymers only formed boundary films if they had a block copolymer structure; statistical copolymers did not form such films. This indicated the requirement for the polymers to adsorb strongly on the rubbing surfaces. As in previous studies it was found that the adsorbed polymer film reduced friction and wear but only in unidirectional sliding – in reciprocated sliding they were much less effective.

3.10 ENGINE EFFICIENCY

Fuel price increases in the 1970s due to Arab-Israeli conflict spurred research into the interest in the development of engine lubricants able to contribute to good fuel economy and ASTM drove research in the direction of understanding how engine lubricants affect engine efficiency [67-71]. In 1984 an ASTM Task Force published a first collective overview of the understanding of high temperature rheology and its effects on engine lubrication [72]. It was found that it is not possible to associate shear thinning behaviour of different polymers to each other. No uniformly accepted model existed. It was concluded that the combination of low and high shear viscosity was responsible for friction and consequently engine efficiency. In bearing experiments it was found that film thickness [73-75] and load capacity [76-79] were in function of HTHS. Hence fuel economy effects were better predicted from HTHS than from kinematic viscosity [80,81].

A significant amount of work has been conducted experimentally to show how VM-containing oils affect engine friction. In an early study in 1977, Bell and Voisey measured engine fuel consumption and wear for a range of model polymer-containing engine oils differing only in the polymer type and the viscosity of the base oil [82]. They also measured how viscosity varied with shear rate up to 10^6 s^{-1} . The authors found that fuel consumption during moderate steady state engine operation correlated with viscosity measured at shear rates of 10^6 s^{-1} and 100°C while bearing and piston ring wear correlated best with viscosity at 150°C and 10^6 s^{-1} and 100°C and $2 \times 10^5 \text{ s}^{-1}$ respectively. Their main conclusion was that a high temperature/high shear rate viscosity should be included in future engine oil classifications.

Galluccio and Koller [83] mapped fuel economy measured using dynamometer bench tests against HTHS 100°C value for oils of different viscosities. Results are shown in figure 3.13 and illustrate a clear reduction in fuel economy with increasing HTHS 100°C . The authors also found that the same VM may be beneficial in one engine but perform very differently and even be detrimental in another, as illustrated in figure 3.14.

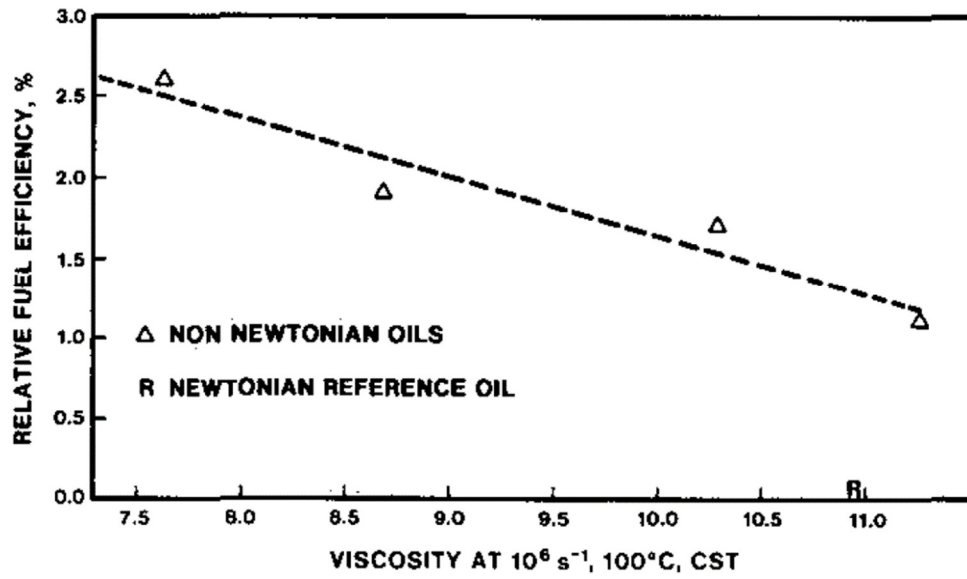


Fig. 3.13: Fuel economy vs HTHS for a 5.7L engine [83]

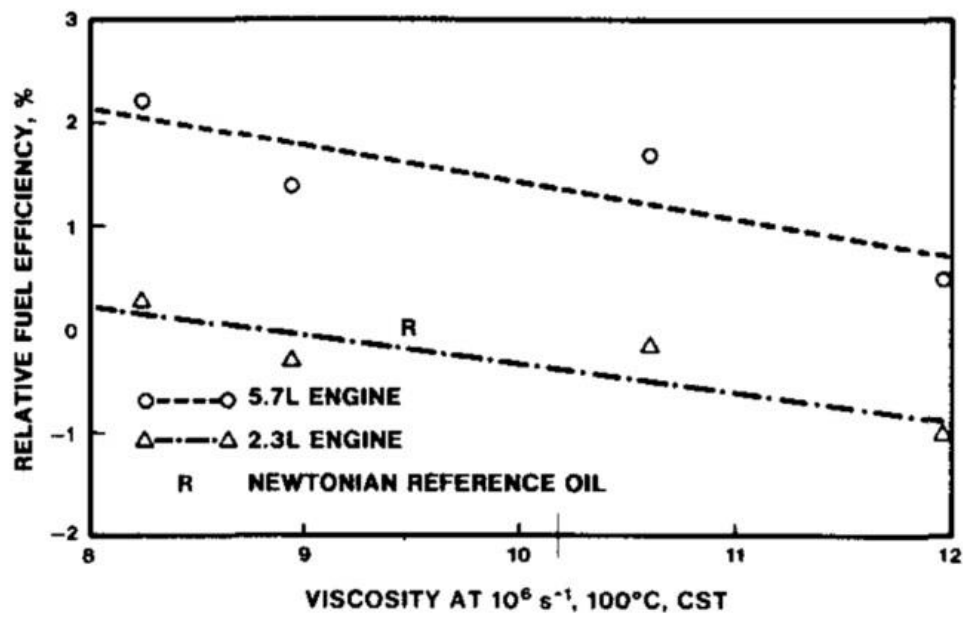


Fig. 3.14: Fuel economy for two engines vs HTHS [83]

Clevenger [84] developed a 2.3l dynamometer bench test suitable to replace the expensive ASTM 5 car test. He also found that multigrade oils were more efficient than single grade ones at the same HTHS100 value. He suggested that the extremely high shear rate in the piston ring (estimated to be 10^7 s^{-1}) contributed to the efficiency improvement of the multigrade oil. This phenomenon was especially noticeable since 65% of the friction was claimed to occur in the piston ring zone.

Vickars and Bates [26] showed that it was also possible to map power savings to viscosity measurements at 150°C and a shear rate of 10^4 s^{-1} (figure 3.10) or fuel saving against kinematic viscosity measurements at 100°C and $4 \times 10^5 \text{ s}^{-1}$ (figure 3.15).

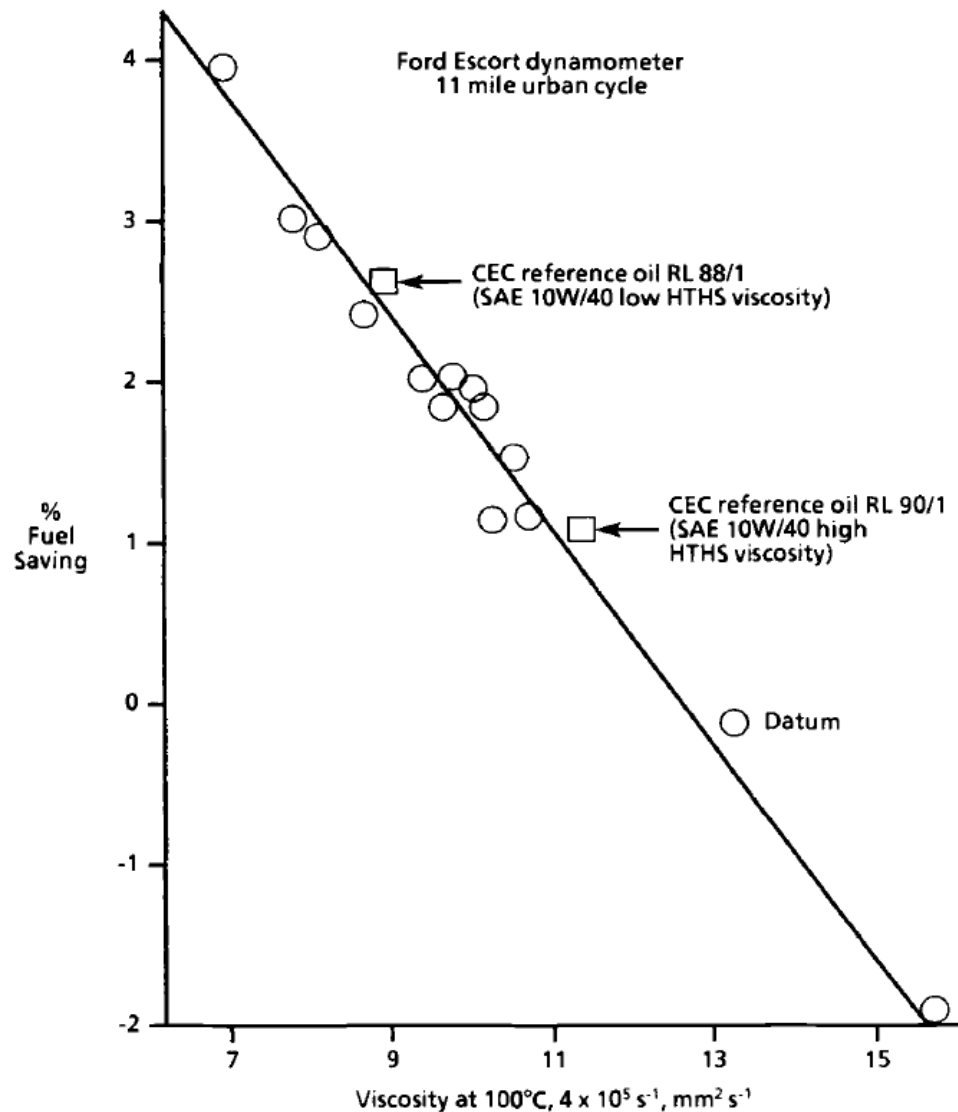


Fig. 3.15: Effect of HTHS on fuel saving [26]

Carvalho *et al* [85] also found quite recently that engine efficiency was linearly correlated with HTHS and that multigrade oils improved engine efficiency *vs* single grade oils.

For gear oils, Bala *et al* [86, 87] found experimentally using a light duty axle efficiency test that a different combination of viscosity and VI was required for optimal efficiency depending on the driving cycle. For low torque and moderate speed, low viscosity and high VI were most efficient while at high torque and also at a combination of low speed and moderate torque an optimised additive package blended in a moderately high VI was most suitable. For moderate to high speed and moderate torque effective additive systems with high VI was recommended.

3.11 ENGINE MODELLING

Although experimental work identified the importance of lubricant shear on engine bearing lubrication in the 1970s it was some time before modelling work was carried out to complement this. Thus in an important review on predictive methods in engine bearing performance in 1983, Martin makes no mention at all of engine oil shear thinning [88]. This is perhaps surprising since hydrodynamic modelling is generally more straightforward than modelling EHD due to the lack of local elastic deformation or significant piezoviscous effects, although accurate engine bearing analysis should take account of overall elastic deformation of the system.

In 1983 Dien and Elrod [89] combined continuity of flow with a viscosity power law shear thinning equation;

$$\eta = m \left(\frac{\partial u}{\partial z} \right)^{n-1} \quad (3.17)$$

to obtain solutions for the pressure field in both thrust and journal bearings. For values of $n > 0.3$ they showed that the velocity profile could be assumed to be linear, in which case a quite simple Reynolds-type solution was possible assuming a mean viscosity through the film thickness according to Eq. 3.17. However for strongly shear thinning fluids when $n < 0.3$, an iterative solution was needed.

Pal *et al* [90] used a similar approach to Dien and Elrod but with a cubic shear stress-strain rate equation, while Gecim [91] used a stress-strain relationship that included a first and second Newtonian.

All of the above authors started their analysis at a stage below the level of approximation of the Reynolds equation by allowing viscosity to vary through the thickness of the film. This makes it quite complex to integrate the flow derivative through the thickness of the film to give a velocity profile and flow rate, as originally described by Dowson [92]. One major simplification is to allow for shear thinning locally in the bearing by evaluating the mean shear rate, $\bar{\dot{\gamma}} = \frac{U_s}{h}$ and then use this to determine a mean local viscosity from a suitable viscosity-strain rate equation. This can then be used directly within the conventional Reynolds equation. Thus viscosity is allowed to vary across the bearing area but not through its thickness. This is equivalent to Dien and Elrod's approximate solution. In 1999 Taylor used this approach to develop a solution for the short bearing approximation including shear thinning [93].

Shear thinning in the piston/line contact has been less widely modelled but Taylor *et al* [94] and Tian *et al* [95] have used the average viscosity through the film approach outlined above to model the piston ring pack and compare results to experimental work. It was found that shear thinning had a significant impact on piston ring pack lubrication. Figure 3.16 illustrates the reduction in friction achieved by shear thinning, with Stribeck curves reminiscent of the schematic ones shown in Chapter 1.

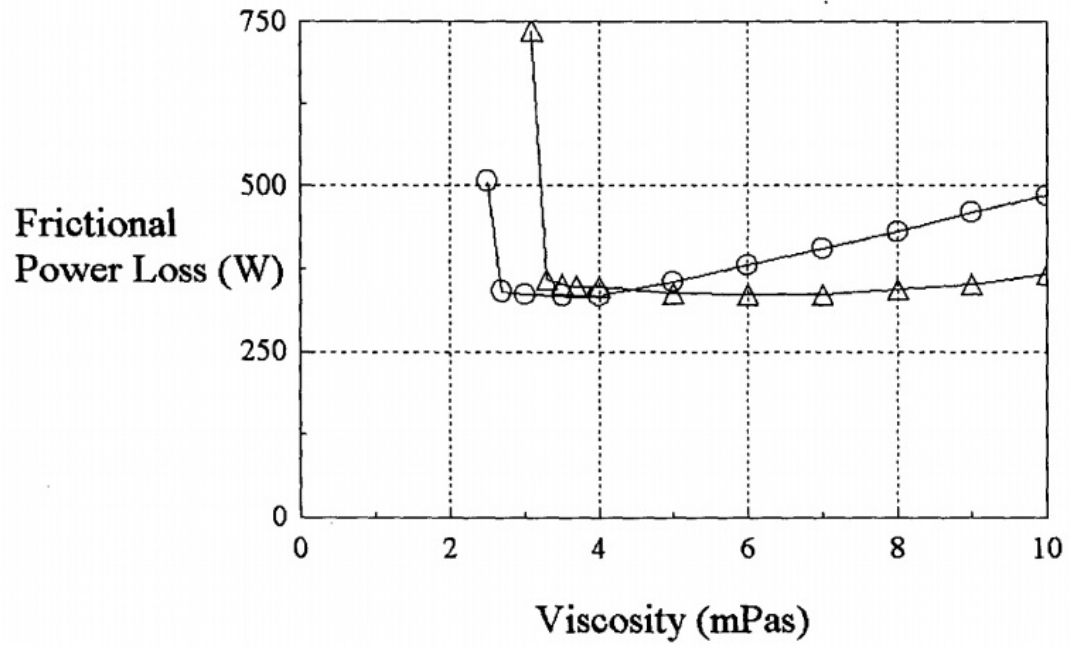


Fig. 3.16: Total ring-pack frictional power loss versus low shear rate viscosity for CAT-1Y73 (1200 rpm, 170 Nm load). Line with circles is the Newtonian result, line with triangles is the result including shear thinning ($\eta_{\infty} = 0.53\eta_0$) [94]

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4 Materials and methods

This chapter describes the material used and experimental methods applied in this thesis. Viscosity modifiers are analysed by gel permeation chromatography while viscosities, densities and flow curves are obtained by a series of viscometers. Methods to produce hydrodynamic contacts are also investigated. Novel techniques for obtaining hydrodynamic film thickness and hydrodynamic friction measurements are presented in Chapters 5 and 6.

4.1 TEST LUBRICANTS

All experimental lubricant test setups are limited in the shear rate range over which they can operate. In order to be able to compare results from the various experiments it is crucial to find an overlap in which lubricant performance can be measured over a measurable shear thinning range. Hence, preliminary calculations of film thickness and friction were made in terms of the lubricant viscosity, the entrainment speed and the contact size. Similar experiments were conducted by Holtzinger in her thesis [1] and her results have been considered in the formulation of the oils used.

For this research it is desirable to choose a polymer with low dispersity, i.e. a low spread of molecular weights. Only a few such polymers are commercially available at reasonable cost, in particular polystyrene and polyisoprene. Holtzinger used both of these and her flow curves suggested better repeatability with polystyrene. Hence polystyrene (PS) was chosen initially for this project as the main viscosity index improver. PS is insoluble in hydrocarbon oils so phthalate esters were chosen as base oils as they fully dissolve this polymer. Various phthalates were chosen to allow for a variation in base oil viscosity; diethylhexylphthalate (DEHP), n-dioctylphthalate (nDOP) dibutylphthalate (DBP) and dimethylphthalate (DMP). Different concentrations of PS could be used to vary the effect of temporary shear thinning while variation in molecular weight allowed control of the shear stress at which a loss in viscosity is observed. Because the PS-phthalate blends have very similar chemical

structures apart from alkyl chain length any observed differences in behaviour could be assumed to originate purely from physical property variations.

Unfortunately, later in the PhD it was found out that phthalate esters are such good solvents that they penetrate the plastics used to generate soft contacts, acting as plasticisers. This meant that the reflective coatings applied to the soft contacts for optical interferometry effectively washed off during film thickness measurements, while fluorescent dye built up within the plastic surface during laser induced fluorescence film thickness measurements. This meant that despite much preliminary work on PS/phthalate ester systems, towards the end of the project the hydrocarbon base oils GTL3, GTL4, GTL8 and squalane and polymers polymethacrylate (PMA), a hydrogenated styrene-diene di-block polymer (HSD di-block), a hydrogenated styrene-diene star polymer (HSD star), polyisoprene (PIP) and olefin copolymer (OCP) VMs were used for the actual study of temporary polymer shear thinning in hydrodynamic lubricated contacts.

GTL3, GTL4 and GTL8 are gas to liquid-derived hydrocarbons with different viscosities as listed in Table 4.2. They are produced from natural gas *via* H₂ and CO using a Fischer-Tropsch synthesis. Table 4.2 also shows the viscometric properties of the other base fluids studied.

PMA, HSD di-block, HSD star and OCP are commercial viscosity modifiers supplied by Shell. In order to facilitate industrial mixing they are supplied in a pre-mixed form, blended in a carrier base oil and antioxidant package. PMA is supplied as 78%wt polymer in a confidential base oil, HSD di-block is supplied diluted in a Group III carrier oil at 8%wt, HSD star is supplied diluted in a Group III oil at 6%wt, and OCP contains 8.5%wt polymer and 91.5%wt carrier oil. The OCP is an ethylene-propylene copolymer with antioxidant in Group II base oil, also described as a hindered alkylphenol ester.

Polyisoprene is a model polymer acquired from Polymer Source Inc (Dorval, Montreal, Canada). It comes in a pure sticky gel type form and can thus be blended without carrier oil or additive package in squalane.

It should be noted that the dilution process in squalane is not as straightforward as for the other blends. The sample was ultrasonicated at 60°C and stirred on a heated magnetic stir bar mixer for which the surface temperature was set to 80°C. The dilution process was not optimised, however the time required for dilution, applying these methods was three days.

Due to these polymers being commercial ones, very limited information was supplied. In order to obtain more information on the polymers supplied, Gel Permeation Chromatography (GPC) was run in the Chemical Engineering Department at Imperial College London. This technique separates different molecular weight components present in the oil. A droplet of blended oil is diluted in 1.5 ml of tetrahydrofuran (THF). A fraction of the mixture is pipetted to flow through a grid of columns. Continuous flow is ensured by flowing more pure THF through the columns. The columns are packed with porous beads that trap the molecules. Molecular weight is determined by retention time. Smaller molecules can enter the pores more easily and thus spend more time being retained by the pores while larger molecules do not enter the pores quite as deep and are washed off more easily by the fresh THF.

In this case the retention time was calibrated using polystyrene for molecular weights between 50k g/Mol and 400k g/Mol. Molecular weights outside of this range may still be measured, however they are not obtained at the peak of the machine's accuracy.

Polystyrene comes in form of linear chains, thus for other types of polymer, such as star polymers or polymers of different adsorption properties, the molecular weight may not be accurately obtained. Usually GPC would be calibrated with an equivalent polymer type to the one tested, however other calibration polymers were not available. Thus all results shown are calibrated against the retention time of polystyrene. The molecular weight obtained in this way is estimated to be of the correct order of magnitude. More importantly, a calibration via polystyrene corresponds to a universal reference. Thus future work is able to reference polymers to the ones used in this thesis, by also calibrating GPC with polystyrene.

Figures 4.1-4.5 show the molecular weights obtained for PMA, HSD di-block, HSD star, OCP and PIP. The lowest molecular weight below 1k g/Mol corresponds in each case to the respective base oil.

For the HSD star polymer in figure 4.3, two peaks are visible. This phenomenon is not unusual for star polymers. It is expected that the smaller molecular weight peak at 100k g/Mol corresponds to single arms while the molecular weight peak at 600k g/Mol corresponds to the star made up of joined arms.

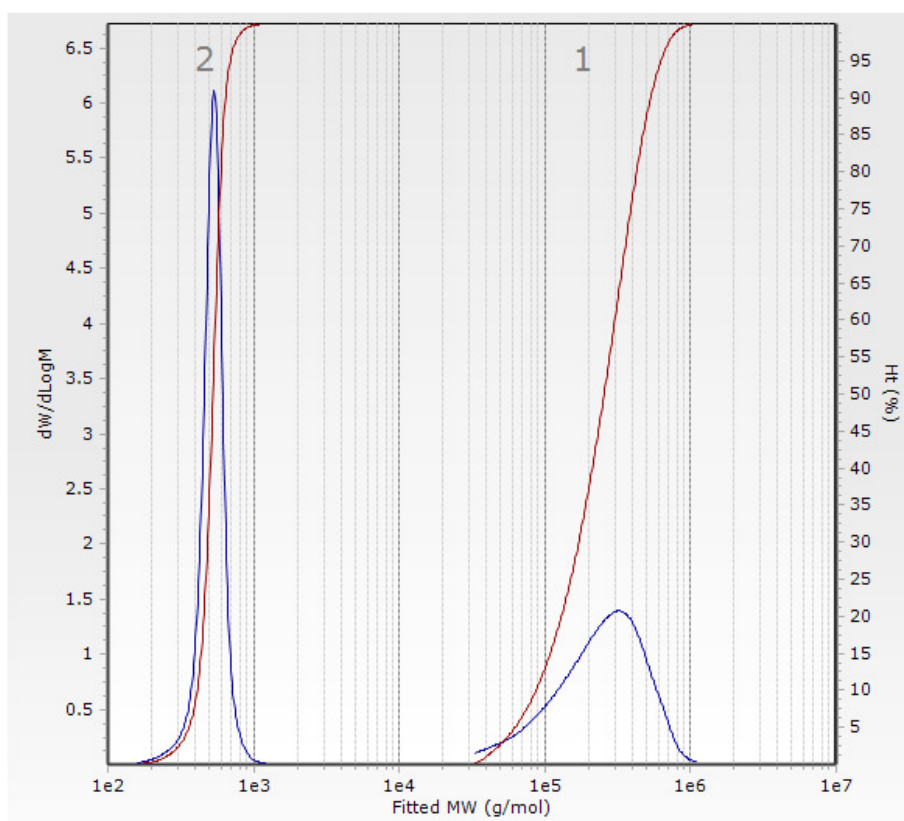


Fig. 4.1: GPC Mwt of PMA (1) and base oil (2), calibrated against polystyrene

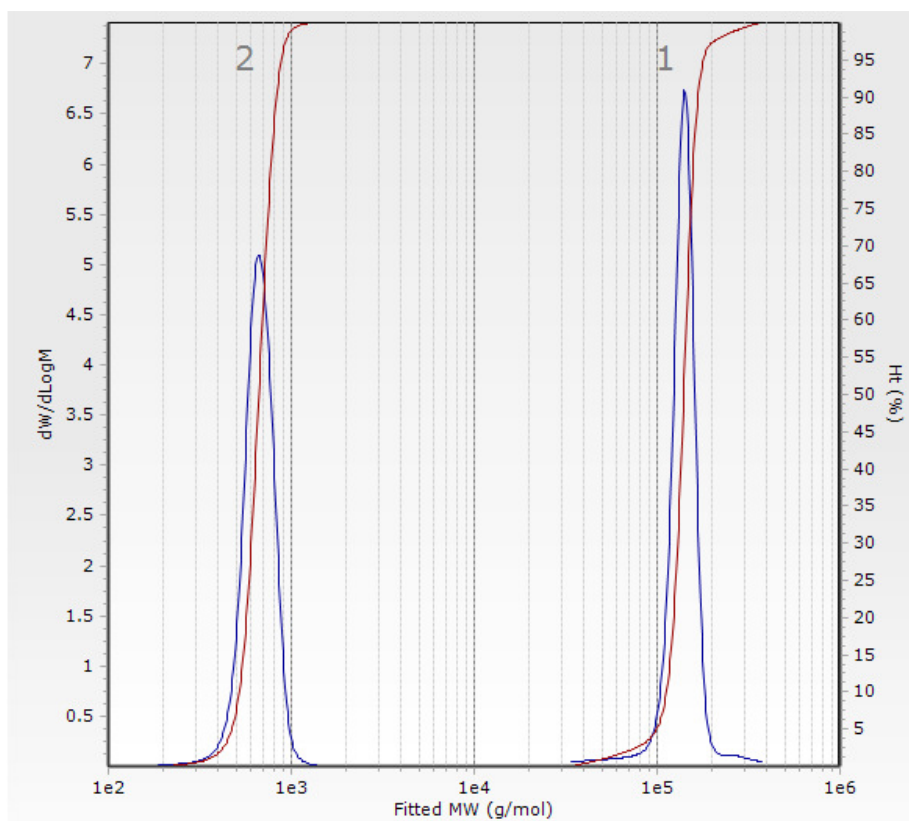


Fig. 4.2: GPC, Mwt of HSD di-block (1) and base oil (2), calibrated against polystyrene

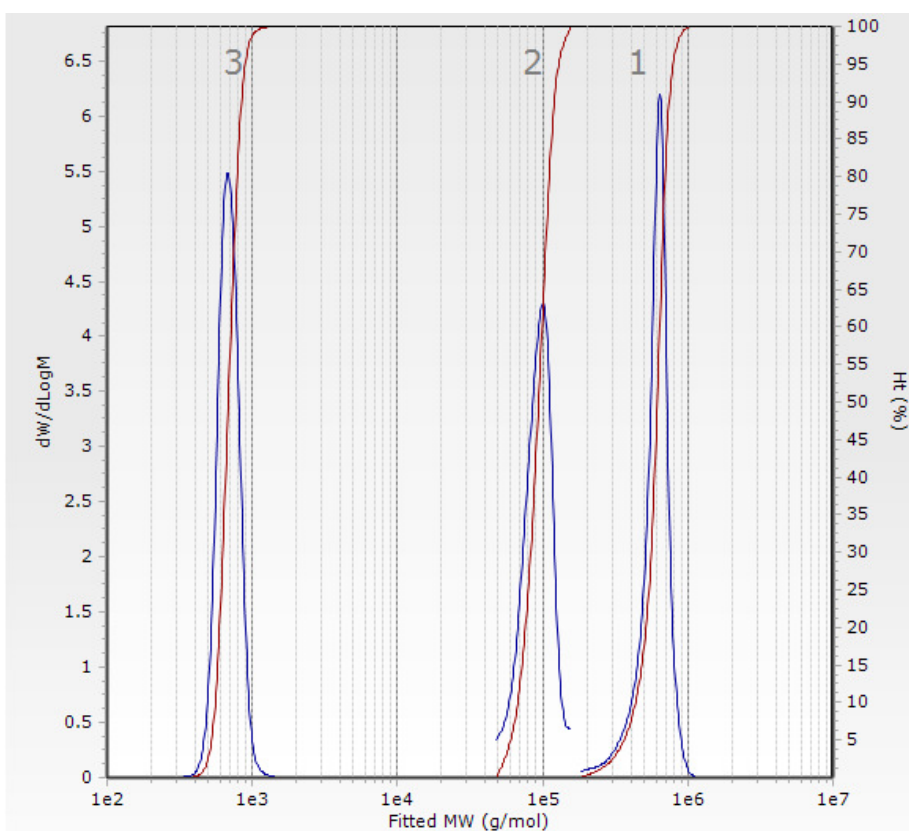


Fig. 4.3: GPC, Mwt of HSD star (1,2) and base oil (3), calibrated against polystyrene

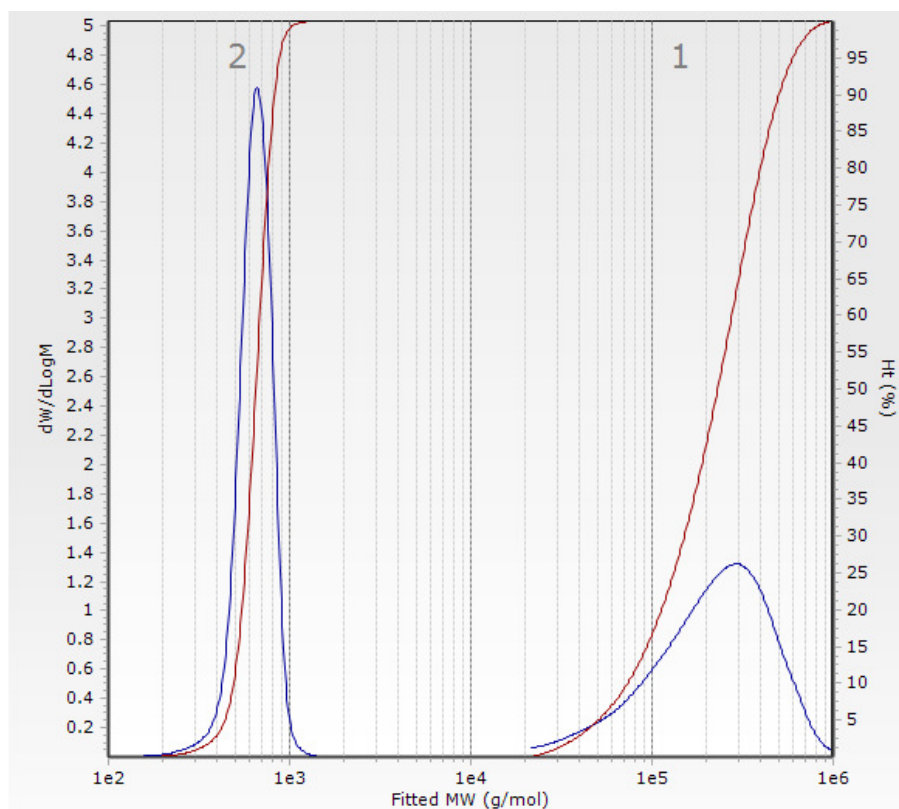


Fig. 4.4: GPC, Mwt of OCP (1) and base oil (2), calibrated against polystyrene

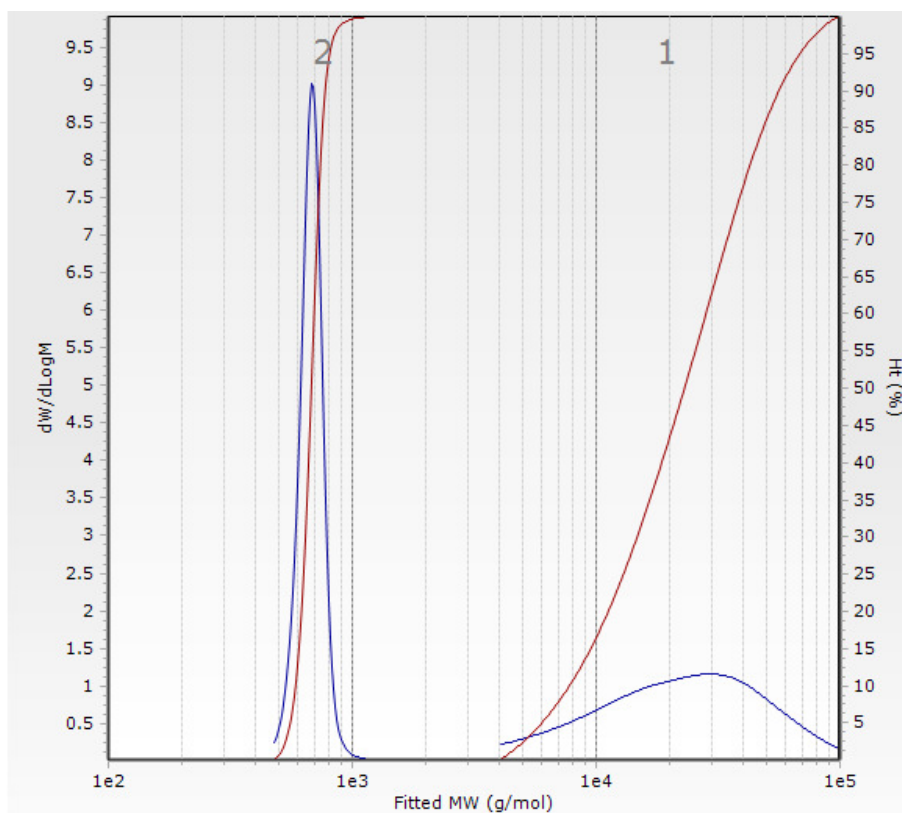


Fig. 4.5: GPC, Mwt of PIP (1) and base oil (2), calibrated against polystyrene

PIP is supposed to be of a molecular weight of 100k g/Mol and not 30k g/Mol as suggested by GPC results in figure 4.5. It is suspected that the severe mixing and heating process during solution has permanently degraded the polyisoprene. Another 3%wt PIP in squalane was prepared, diluted to 80%wt in di-ethyl-hexyl sebacate. Di-ethyl-hexyl sebacate increases the polarity of the bend and thus improves the dilution process. As a result this batch underwent less severe conditions in order to dissolve. It was not ultrasonicated, but only stirred for a few days on a heated magnetic stir plate at 60°C bottom surface temperature. Unlike the previous solution, this one did not change colour.

Figure 4.6 shows the GPC result for this new solution.

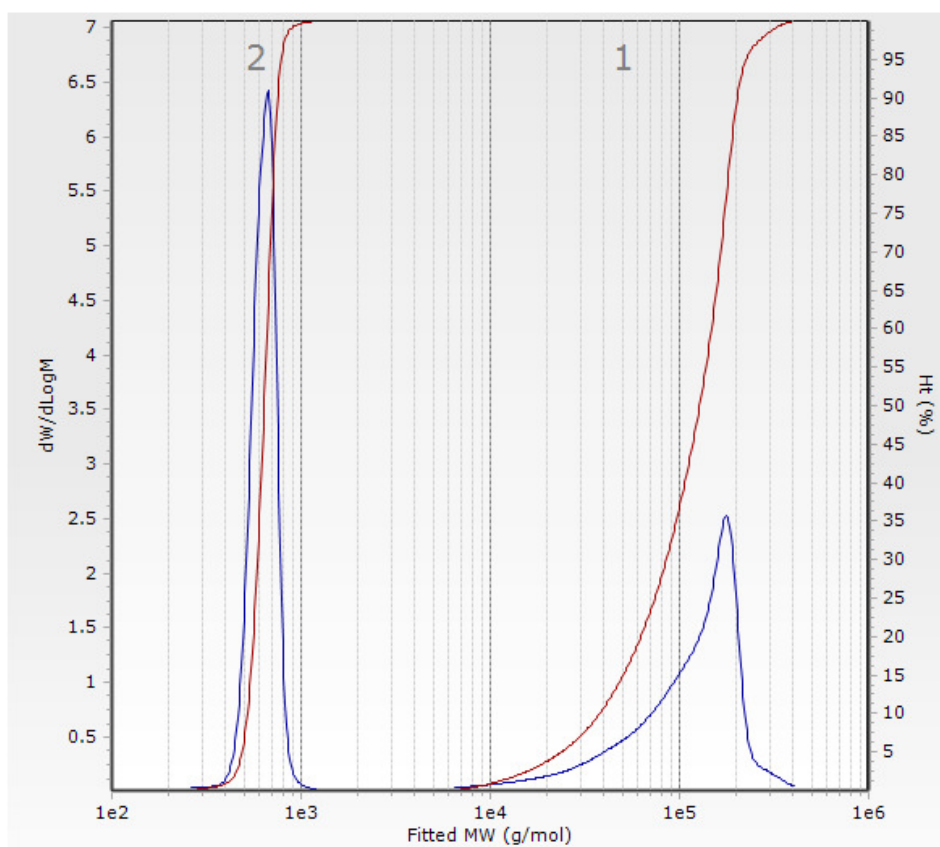


Fig. 4.6: GPC, Mwt of PIP-polar (1) and base oil (2), calibrated against polystyrene

The molecular weight of this solution appears much higher, with its peak at 130k g/Mol.

Unfortunately due to limited quantity available and the high cost of polyisoprene, the large, degraded batch from figure 4.5 had to be used in experiments in Chapter 7.

Table 4.1 displays the polymer properties obtained from GPC experiments for all VMs.

Table 4.1: VM properties

	Peaks	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
PMA	Peak 1	320720	178496	287105	395697	490593	381124	1.61
	Peak 2	533	503	526	547	569	544	1.05
HSD di-block	Peak 1	140457	132610	140446	147618	156650	146458	1.06
	Peak 2	666	643	670	695	719	691	1.04
HSD-star	Peak 1	641325	568526	603101	629558	651506	626071	1.06
	Peak 2	100803	89281	94034	98592	102938	97931	1.05
	Peak 3	675	674	693	713	734	710	1.03
OCP	Peak 1	293567	152474	263547	374051	469770	359333	1.73
	Peak 2	661	622	655	684	712	680	1.05
PIP	Peak 1	29215	16594	27875	41281	53145	39434	1.68
	Peak 2	685	672	681	690	699	688	1.01
PIP - polar	Peak 1	176520	74208	126314	161045	186639	157004	1.70
	Peak 2	670	623	638	653	668	651	1.02

GPC and lightscattering results on polystyrene and polyisoprene supplied by the polymer supplier companies may be found in Appendix 10.2.

Table 4.2 displays the properties of the base oils and Table 4.3 presents the properties of the VM improved oils implemented.

The oils in table 4.3 were blended as follows: the lower concentration OCP blend, the HSD di-block blend and the HSD star blend were iterated in order to thicken a Newtonian GTL4 oil to a low shear viscosity oil of a Newtonian GTL8 oil.

The lower concentrated PMA blend was mixed in order to thicken a Newtonian GTL3 oil of lower viscosity than GTL4 to a GTL8 blend. GTL3 was chosen in order to increase the polymer content and in order to increase the ability to shear thin.

In order to increase shear thinning ability further, a high concentrated blend of OCP and a high concentrated blend of PMA were mixed without a target low shear viscosity in mind. For the PMA blend the concentration was doubled while for the OCP blend the concentration is nearly five times the lower concentrated blend.

Polystyrene blends and polyisoprene blends were mixed to concentrations allowing for a good amount of shear thinning while limiting the amount of polymer implemented in order to reduce cost.

Table 4.2: Base oils

	Viscosity 40°C (cP)	Viscosity 100°C (cP)	Density 40°C(g/cm ³)	Density 100°C(g/cm ³)	VI (ASTM D2270)	Refractive Index
GTL 3	7.97	2.06	0.79	0.75	112.5	1.445
GTL 4	14.77	3.08	0.80	0.76	142.0	1.450
GTL 8	35.86	5.93	0.81	0.78	131.6	1.455
DEHP	26.04	3.91	0.97	0.92	18.8	
Squalane	15.13	3.15	0.80	0.76	122.0	1.447

Table 4.3: Densities and low shear rate viscosities of the VM improved blended oils

	Viscosity 40°C (cP)	Viscosity 100°C (cP)	Density 40°C (g/cm ³)	Density 100°C (g/cm ³)	VI (ASTM D2270)	Refractive Index
14%wt PMA & 3.95%wt carrier oil in GTL 3	38.98	7.97	0.80	0.76	211.5	1.448
28%wt PMA & 7.9%wt carrier oil in GTL 3	174.25	28.08	0.81	0.77	219.8	1.451
0.88%wt OCP & 9.46%wt carrier oil in GTL4	36.05	6.85	0.80	0.77	185.0	1.451
4.24%wt OCP & 45.75%wt in GTL4	710.94	87.19	0.82	0.78	229.8	1.454
1.53%wt HSD di- block & 17.58%wt carrier oil in GTL4	35.92	7.12	0.81	0.77	197.3	1.450
1.64%wt HSD star & 25.66%wt carrier oil in GTL4	35.42	7.47	0.81	0.76	222.2	1.451
3%wt 100k g/Mol PIP in Squalane	20.95	4.22	0.80	0.76	156.4	1.447
5%wt 50k g/Mol PS in DEHP	n.a.	9.12	n.a.	n.a.	n.a.	n.a.
10%wt 50k g/Mol PS in DEHP	213.16	20.31	0.98	0.93	119.9	n.a.
4%wt 100k g/Mol PS in DEHP	75.67	9.84	0.97	0.93	121.7	n.a.
2%wt 200k g/Mol PS in DEHP	56.88	8.20	0.97	0.93	127.3	n.a.
5%wt 50k g/Mol PS in DMP	n.a.	5.17	n.a.	n.a.	n.a.	n.a.
10%wt 50k g/Mol PS in DMP	n.a.	11.23	n.a.	n.a.	n.a.	n.a.

4.2 TEMPORARY SHEAR THINNING CURVES

4.2.1 CALIBRATION VIA SVM 3000 MEASUREMENTS

The Stabinger Viscometer (SVM) shown in figure 4.7 and manufactured by Anton Paar (St. Albans, United Kingdom) was chosen to measure the low shear rate viscosities of the test lubricants. This is a horizontal concentric cylinder device in which an outer cylinder is rotated steadily, a free-floating inner cylinder is braked electromagnetically and the torque is measured using an eddy current method. The shear rate is not precisely defined and depends on the fluid viscosity but is in the range 1 to 10^3 s^{-1} .



Fig. 4.7: Stabinger Viscometer SVM 3000 [2]

Anton Paar supplies calibration oils for this device but these are relatively expensive. Therefore, within this project more widely available Newtonian oils were purchased and measured in order to replace previously-used reference oils. Squalane and DEHP were selected for this purpose since these can be purchased from chemical companies in pure form at a reasonable price and are unlikely to become unavailable in future. These oils could then be used to calibrate the other experimental viscometer setups, the

rheometer, mid-shear developments and USV. It should be noted that DEHP requires careful handling and disposal for safety reasons.

The accuracy of the SVM was found to be dependent on meticulous cleaning and re-calibration of the SVM following each measurement. Furthermore it was noted that the cleaning solvents toluene and isopropanol have an effect on the first measurement regardless of the amount of oil used for measurement. Whereas the offset is small, it is recommended to run three tests with one oil without cleaning with toluene and isopropanol in between these tests. Between each test it is important to flush approximately 2 ml of test oil through the pipe feed system of the SVM. Approximately 10 ml of oil is thus required to obtain an accurate measurement.

The cleaning method suggested by the manufacturer does not ensure satisfactory repeatability. It is possible that some of the polymer-containing oils left a residue which is difficult to remove and affects subsequent measurements. In order to obtain very high precision, it was found necessary to dismantle the apparatus and clean the rotor and stator in toluene and isopropanol in an ultrasonic bath before testing.

Shear rates at which the viscosity is measured with the SVM lie between 10 and 10^3 s^{-1} , however the user is not able to control the shear rate. Fortunately it is believed that the polymer solutions studied do not show any shear thinning up to 10^3 s^{-1} . Table 4.4 displays temperature scan viscosity measurements of squalane, and DEHP to a precision of 99.4%. Precision was determined by comparing to a supplied reference oil from Anton Paar.

Some of the polymers used in this project are quite expensive and therefore not all blends were measured using the SVM due to the amount of oil that would be consumed for this measurement. The rheometer described in the next section is able to measure viscosity sufficiently accurately at user specified low shear rates when correctly calibrated against the reference oils measured by the Stabinger.

Table 4.4: New reference oil data (error margin based on APN 26 viscosity standard deviation)

	Squalane	DEHP	
T[°C]	η [cP]	η [cP]	Error margin [%]
20	35.75	77.65	-0.19
40	15.13	26.04	0.39
60	7.86	11.62	0.48
80	4.69	6.27	0.04
100	3.15	3.91	0.60

4.2.2 LOW TO MID SHEAR RATE RHEOMETER

A TA Instruments Hybrid rheometer (New Castle, Philadelphia, United States of America) was available. As supplied this includes several possible geometries and strain rate ranges and initially the limits in strain rate and precision of the various geometries were explored. The strain rate is limited because centrifugal forces enhance lateral leakage in most configurations. The Newtonian oils squalane and DEHP were employed to verify the precision in viscosity measurement for a given geometry. Three geometries were investigated: flat on flat (figure 4.8), concentric cylinders (figure 4.9) and cone on plate (figure 4.10).

1. Flat on flat:

The zero gap setting of the rheometer in a flat disc on flat configuration is not precise enough to allow for accurate viscosity measurements for gaps below 500 μm . However, the low viscosity of the oil meant that there was insufficient torque for accurate measurements for film gaps greater than 200 μm . Furthermore, very small gaps in the order of 20-50 μm are required to obtain high shear rates. To overcome this, it is possible to rectify the measurements obtained at the extremely small gaps by interpolation, as long as the oil in the contact behaves Newtonian-like at the given shear rate. This provides interpolation equations which should be applicable to some extent to non-Newtonian lubricants, as was done by Holtzinger [1] to obtain viscosity measurements at shear rates up to 10^4s^{-1} . However further experimental work in the current study cast doubt on the accuracy of this approach. Lateral leakage and also high

fluctuations in the measurements were observed and the interpolation inaccuracy blurs the experimental data and makes it difficult to identify the precise location of the onset of shear thinning. Hence this geometry was considered unsuitable for this study.

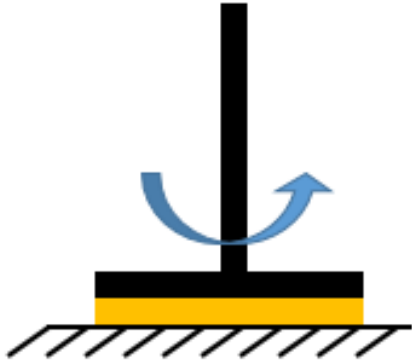


Fig. 4.8: Flat on flat geometry

2. Concentric cylinders:

The concentric cylinder geometry allows measurement of the lubricant's viscosity accurately without gap settings in the shear rate range of $10\text{-}10^2\text{ s}^{-1}$. At higher shear rates, viscosity measurements fluctuate as bubbles form in the lubricant. This geometry is very limited in shear rate range and requires a high quantity of lubricant with no benefits over the SVM.

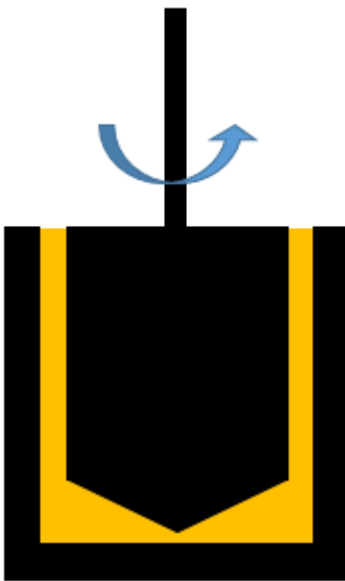


Fig. 4.9: Concentric cylinders

3. Cone on plate:

The cone-on-plate geometry appears to measure viscosity most accurately over a reasonably large shear rate range before centrifugal forces and lateral leakage affect measurements. It was found that a bottom peltier plate with a larger diameter than the cone helped counteract lateral leakage without affecting the viscosity measurement.

Repeatability and precision with the cone on plate geometry for shear rates from 10 and 10^3 s^{-1} were found to be $\pm 3\%$. Some results are included in figures 4.12-14. The advantage of this rheometer over the SVM is that the strain rate is known precisely and can be varied.

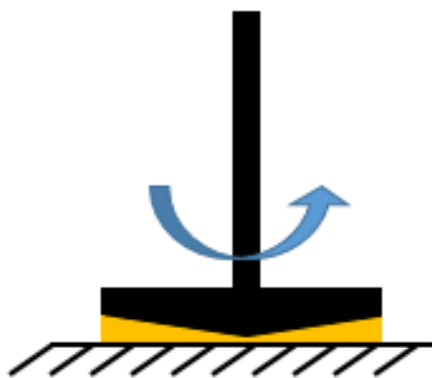


Fig. 4.10: Cone on plate geometry

4.2.3 HIGH SHEAR RATE VISCOMETER: USV

The PCS Ultra Shear Viscometer is a concentric cylinder viscometer able to measure viscosity in the shear rate range of 10^6 - 10^7 s^{-1} . The maximum torque this machine can measure at these shear rates is, however, limited. Therefore oils must be selected with sufficiently low viscosity not to exceed the torque limit.



Fig. 4.11: Ultra Shear Viscometer (USV) [3]

The USV (figure 4.11) is based on a concentric cylinder geometry with a very small gap of typically $1.3 \mu\text{m}$. Normally viscometers with such geometry are limited to a maximum strain rate of $ca\ 10^6\ \text{s}^{-1}$ since above this level temperature rise due to shear heating becomes excessive. In the USV this problem is overcome by using a very short shearing time to ensure any such temperature rise is very small. A motor accelerates a flywheel to high speed and then a clutch system engages to transmit the rotational energy to the inner cylinder (rotor) for as short time at set shear rate. Torque is measured and averaged over just 8 rotations of the cylinder. Depending on the lubricant viscosity and thus the shear stress applied, a small amount of shear heating can still occur within this time frame but the USV is able to measure the increase in temperature on the stator and, using heat transfer theory, estimate the temperature rise within the contact. The temperature of the chamber is then reduced slightly using this temperature offset to ensure that the lubricant sample reaches the sought test temperature just when the viscosity is measured.

In the USV a series of engagements is generally made; one to obtain the temperature offset and then three consecutive engagements for measurement. A torque sensor is fitted to the outer concentric cylinder (stator) and the average measurements of the last three engagements are used to determine a viscosity value.

In this project considerable development work was carried out in order to maximise the precision of the instrument and to enable it to be used reliably with shear thinning polymer solutions. This included some redesign of the instrument to reduce contamination, selection of new reference liquids and the development of test protocols with stringent cleaning and operational procedures.

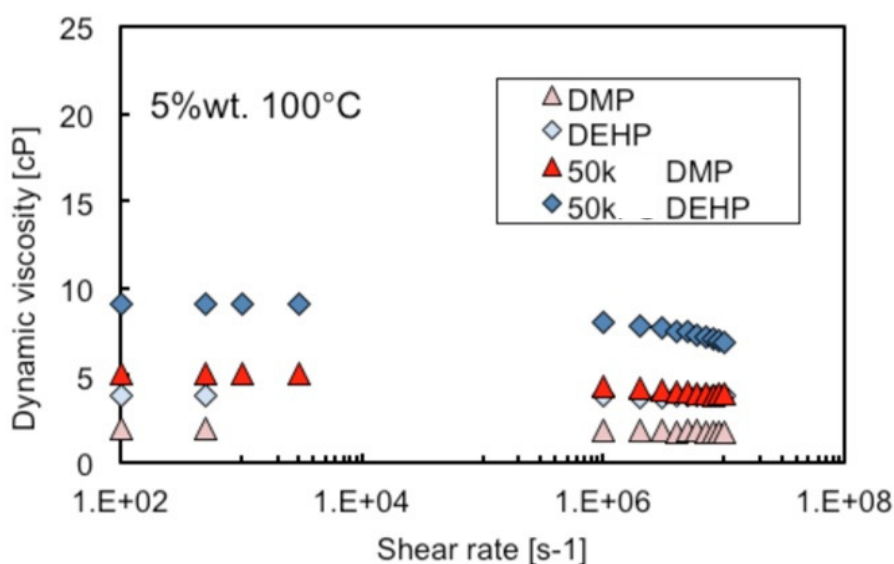
It was found that the clutch of the USV exhibited continuous wear to produce fine metallic particles that contaminated the solution and affected viscosity measurements over long periods of testing (100 shear passes or more). A “dust catcher” was therefore designed and 3D-printed to seal off the source of contamination. Measurement techniques and calibration techniques described below were then developed in this project to obtain accuracies of viscosity measurements of 99%: For this study, two commercially available USVs supplied by PCS were equipped with the latest software updates and several gap geometries were studied side by side. PCS Instruments themselves sponsored and supported this undertaking.

Several aromatic phthalate esters, 99% pure squalane (Sigma Aldrich - St. Louis, United States of America) and Tannas reference oils (Midland, United States of America) were used as Newtonian model fluids.

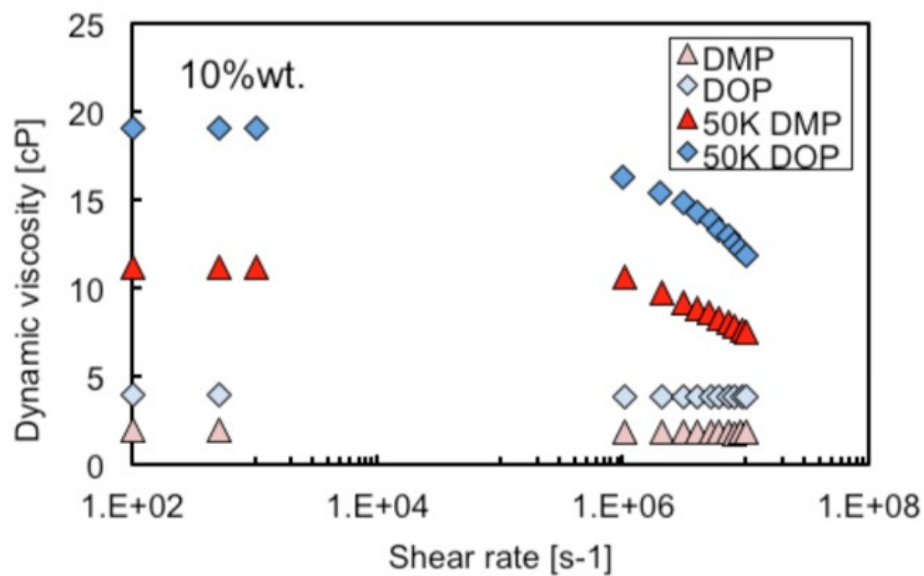
Phthalate esters performed best as reference oils, since they did not degrade and their ability to dissolve most viscosity modifiers is ideal to flush clean a mechanical system. However the health and safety requirements of these fluids, including the need to wear a protective mask, make these oils impractical for commercial use. Squalane is therefore recommended. This performed just as well as the phthalate esters though possible degradation required the mechanical system to be cleaned by solvents between use; a procedure that is anyway recommended between each test in order to obtain the best possible results. The Tannas oils appeared to permanently shear thin.

The protocol described in Appendix 10.1 was developed in order to maximise accuracy of measurement in this project and enable 99% precision. It is recognised that this is not practical in routine commercial use since it is time-consuming and skilled labour intensive. However even partial application of the recommended steps should greatly improve precision.

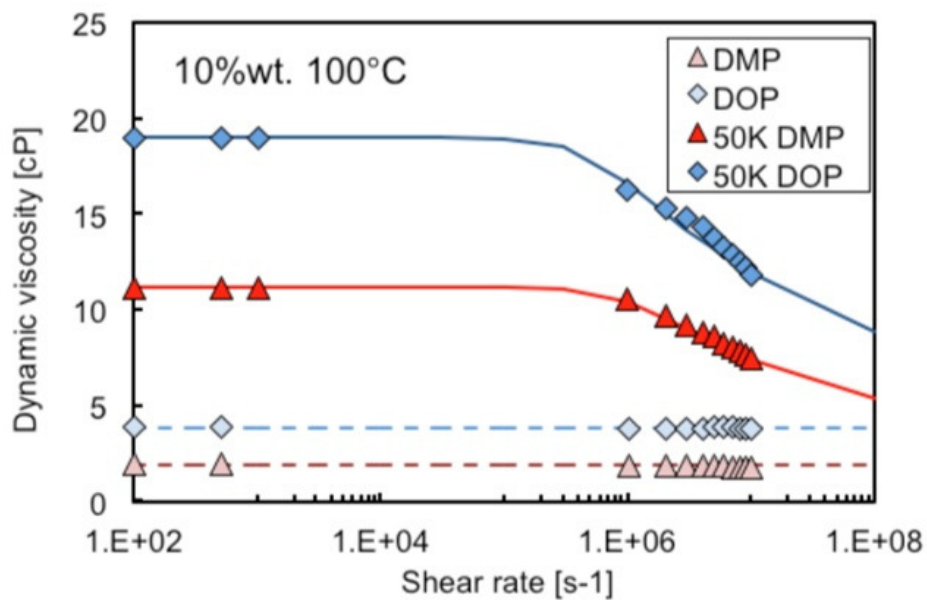
Figures 4.12 and 4.13 show flow curves implementing the rheometer and USV. Figure 4.14 fits the Carreau-Yasuda model to the 10% concentrated polystyrene in DEHP flow curves.



***[4] Fig. 4.12: Viscosity over a wide shear rate range for 2%wt. PS at 100 °C



***[4] Fig. 4.13: Viscosity over a wide shear rate range for 10%wt. PS at 100 °C



***[4] Fig. 4.14: Carreau Yasuda equation fits to viscosity-shear rate results for 10% wt. PS solutions

4.2.4 MID SHEAR USV EXTENSION

As can be seen in figures 4.12-4.14 the rheometer and the USV only partially span the flow curve. In order to measure viscosity at shear rates of $10^4 - 10^6 s^{-1}$ another viscometer is required. Currently there are no test rigs available on the market that measure viscosity in the mid shear rate range reliably while using small amounts of lubricant. Therefore, the development of such a test rig was sought.

Several rigs were developed within this work. The ones that were started but not taken through to completion are described in Appendix 10.2.

A relatively straightforward approach is to use a large gap geometry in the USV. PCS Instruments had tried to develop this method in the past unsuccessfully. A combination rotor and stator with a gap of $15\text{ }\mu\text{m}$ was obtained (about 10x the normal gap) and tested. The main problems that were found to arise with such a geometry were vibration of the rotor and possibly cavitation. These occurred randomly or at certain speeds, probably due to resonance. Hence, it was not possible to automate data acquisition and this is most likely the problem PCS Instruments had in development. It was however possible to use PCS Instrument software to manually apply shear passes and manually change the test conditions. With some care this enabled mid-range shear rate data to be obtained by avoiding speeds at which instability occurred. The number of revolutions over which a measurement is taken is a particular useful factor to adapt according to conditions. The user must monitor the force trace of the engagement and practice with Newtonian oils is recommended in order to assess the settings for each shear rate. It is possible to reduce the error margin below 5% by applying the correct settings for the shear rate range of $5 \times 10^4 - 5 \times 10^5 s^{-1}$.

Results using this manual control method are shown in figure 4.15. For lower viscosity oils, the instrument is unable to produce stable results at the lowest shear rates. This is most likely due to cavitation and reduction in vibration damping.

Other mid shear viscometers were developed, though have been discarded due to reduced practicality when compared to the large gap geometry solution. For further

information on the abandoned attempts on the development of these viscometers the reader is referred to Appendix 10.2.

4.2.5 COMPLETE FLOW CURVES

Figure 4.15 shows combined results from rheometer, USV and the large gap USV for 2% wt. 200k MWt polystyrene in DEHP at 40C and 60C. Also present on the plot are flow curves without the mid shear data for 10% wt. 50k MWt and 4% wt. 100k MWt. polystyrene in DEHP. USV data and rheometer data alone already enable the Carreau-Yasuda (CY) equation to be fitted. The mid shear data from the 2% Wt. 200k MWt solution falls on the theoretical CY map.

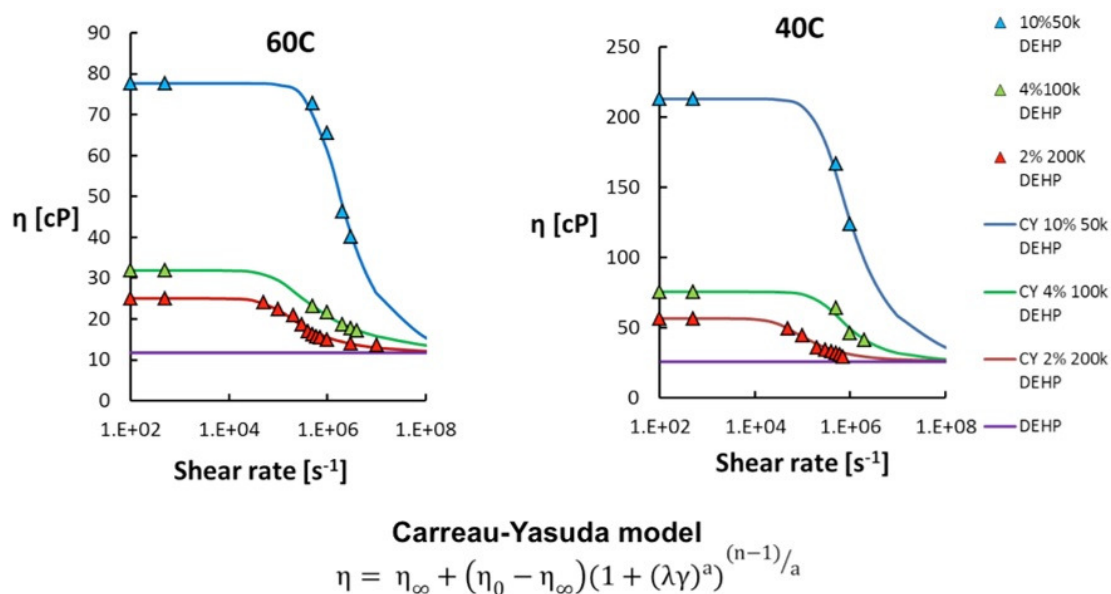


Fig. 4.15: Complete flow curve for 2%wt. 200k MWt PS in DEHP compared to partial flow curves for 10% 50k PS and 4% 100k PS in DEHP

4.3 MODEL HYDRODYNAMIC CONTACTS

In crankcase engines, two of the lubricated components of interest, the piston ring/liner and the connecting rod plain bearings, operate largely in the hydrodynamic lubrication regime. These components are also responsible for a high proportion of the friction losses in an engine. Therefore to research the effect of polymer shear thinning of viscosity modifiers on engine lubrication a model hydrodynamic contact is required. Moreover, in order to be able to distinguish accurately the effects of shear thinning it is desirable to avoid piezoviscous effects, which means that a low pressure, hydrodynamic contact is needed.

There are two ways of obtaining such a low pressure contact. The first is to use a conforming geometry as is present in journal bearings and piston rings. However this type of geometry is difficult to align and requires high applied loads if the contact has macro-scale dimensions. Both are quite difficult to achieve in laboratory conditions. Therefore, as mentioned in Chapter 3, most experimental research on hydrodynamic friction has used an actual hydrodynamic bearing configuration.

An alternative approach is to use a soft EHL contact. This uses a non-conforming contact such as a ball on flat where one or both of the surfaces has a low elastic modulus, such as a deformable plastic ball against a glass disc. Elastic deformation of the ball keeps the contact pressure low so that piezoviscous effects are eliminated or minimized, while the ball on disc geometry is self-aligning. The contact operates in isoviscous-elastic hydrodynamic conditions.

To facilitate this approach research was carried out in this study to manufacture ball and disc specimens made from plastic materials. Lubricated polymeric contacts have been considerably studied in the past but the majority of research has been carried out on elastomers such as rubber and polydimethylsiloxane (PDMS). However such elastomers have elastic moduli typically in the range 1 to 10 MPa, which results in a very highly deforming contact which cannot operate in thin film, very high strain rate conditions. The interest in the current study was in plastic polymers with elastic moduli

in the range around 1 GPa. These still operated in isoviscous-elastic conditions but the smaller contact sizes enable thinner fluid films and thus higher strain rates.

4.3.1 PLASTIC HEMISPHERES

Various epoxies, polymethacrylate and polyurethane samples were cured in concave glass lenses in a similar manner to that described by Holtzinger [1]. The difficulty in this method is releasing the polymer hemisphere from the lens mould. Release solvents would affect the roughness of the product since a thin film cured onto the lens would not be uniform. Direct curing without a release interlayer resulted in broken or rough polymer hemispheres since parts of the polymer hemisphere surface stuck to the mould and remained there after the demoulding process.

To address this problem a non-stick mould material, polydimethylsiloxane (PDMS) was identified and it was found that all polymers tested were able to fully cure in a PDMS mould and allowed simple demoulding. Furthermore, PDMS itself demoulds easily from glass.

Thus a two-stage technique was developed in which PDMS moulds were produced using convex glass lenses and perfect hemispheres of the polymers of interest were cured inside these. It was noted that strongly exothermic curing polymers or polymers requiring heat would deform the PDMS mould slightly due to thermal expansion. Thus polyurethane was identified as the best polymer for use since it cures at room temperature.

4.3.2 PLASTIC BALLS

In addition to not adhering to either glass or plastics, PDMS has the very useful property of very low Young's modulus, and thus being able to undergo large amounts of elastic deformation without permanent loss of shape. It was thus possible to produce a PDMS ball mould from a glass ball and cast a polyurethane ball in the PDMS mould. A 19.06 mm diameter polyurethane ball thus produced is shown in figure 4.16.

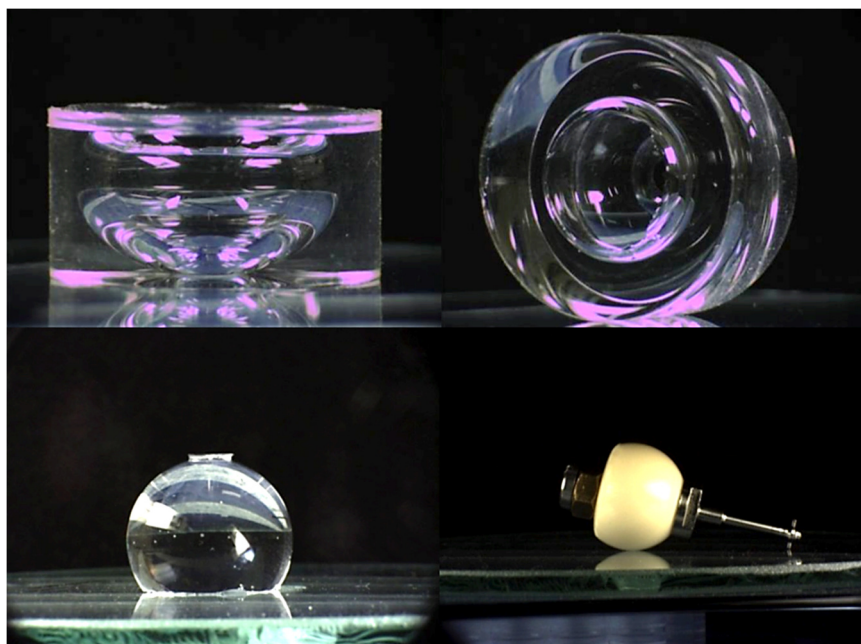


Fig. 4.16: PDMS moulds, PU waterclear and PU balls, 19.06mm in diameter

4.3.3 PLASTIC DISCS

Polyurethane is commercially obtainable in both, transparent (also known as *polyurethane waterclear*) and opaque versions. Since it was intended to use optical interferometry with a steel ball on transparent plastic disc, the transparent polymer was preferred to make plastic discs. The procedure was as follows.

A PDMS disc mould was prepared by casting PDMS around a flat ground smooth glass disc. The mould itself was cast inside a cylindrical glass container in order to ensure that the highly flexible PDMS would remain undeformed once the glass disc is removed and the PU cast inside the PDMS mould.

*** [5] Waterclear PU3660 part A and part B supplied by Alchemie Limited (Warwick, UK) were thoroughly mixed together and degassed before the mixture was poured into the PDMS mould. Several small batches were mixed separately at the same time, since mixing a too high volume of PU resulted in self heating (thus too fast curing) and increased degassing time. Even though initial full hard curing time at room temperature was less than 24h, it was found necessary to leave the PU in the mould for 4 days to avoid deformation of the disc during the demoulding process. Furthermore, once

demoulded, discs were left on a flat PDMS surface for 24h in order to ensure full strength of the edge thickness and another 24h inverted to allow for the contact surface to fully strengthen. This process gave roughness similar to that of the original glass disc and below the measurable roughness range of the white-light interferometry Veeco measuring device ($R_a < 10\text{nm}$, measurement value $< 2\text{nm}$).

Polymer discs in other transparent plastic materials were manufactured from sheets of the polymers obtained directly from manufacturers. Polymethylmethacrylate (PMMA) (10 mm thick) was obtained from “Cut Plastic Sheetting” (Ivybridge, United Kingdom) and polycarbonate (PC) (9.5 mm thick) from “The Plastic Shop” (Coventry, United Kingdom). These were cut into circular discs by turning and milling on a lathe. Discs of 100 mm diameter could also be economically obtained from “Cut Plastic Sheetting”. Thus only the centre hole for the shaft had to be manufactured. The manufactured discs were then sent to PCS Instruments in order to be coated with a 20 nm thick semi reflective chromium layer. Figure 4.17 shows a coated PMMA disc (left) and a coated PC disc (right).

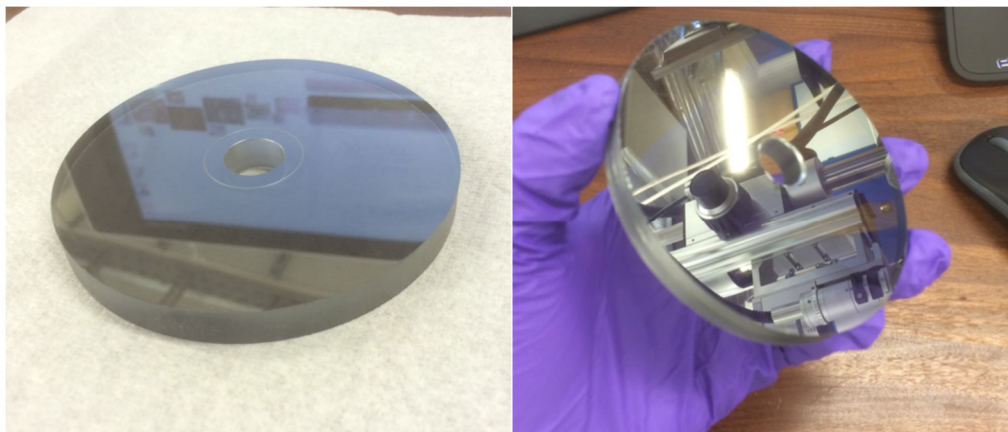


Fig. 4.17: Coated polymer discs, 100mm in diameter

References

- [1] Holtzinger, J.: Influence of viscosity modifiers on hydrodynamic friction. PhD Thesis, Imperial College, (2012)
- [2] <https://www.winelightanalytical.com/anton-paar.php>
- [3] <http://pcs-instruments.com/products/>
- [4] Marx, N. Taylor, R.I., Spikes, H.A.: Influence of polymer shear thinning on friction in hydrodynamic contacts. Tribo BR Second International Brazilian Conference on Tribology, 3-5 November 2014, Foz do Iguau Paran, Brazil, (2014)
- [5] Marx, N., Guegan, J., Spikes, H.A.: Elastohydrodynamic film thickness of soft EHL contacts using optical interferometry. Tribology International 99, pp.267-277, (2016)

5 Measurement of hydrodynamic film thickness in soft contact

This chapter describes the development of two techniques for measuring and mapping hydrodynamic film thickness in soft contact. From this an optical interferometry method is selected, involving the use of a coated polymer disc, to carry out further measurements. It is used to measure film thickness as a function of entrainment speed, sliding speed and load for two base oils of different viscosity. The results are compared to existing computer-model derived soft EHL film thickness equations and a modified such film thickness equation is proposed. This optical interferometry technique will be applied in Chapter 7 to measure the film forming properties of shear thinning polymer solutions.

5.1 INTRODUCTION

The problems of establishing a conforming sliding contact to study hydrodynamic film formation has already been discussed in Chapter 4. In this study these problems were avoided by using a ball on disc contact where one of the surfaces was made of polymer and thus had much lower elastic modulus than steel. This formed a “soft-EHL” film in which the pressure was so low that there was no significant pressure-viscosity effect, at least in the inlet where it would affect the film thickness. Thus the film thickness should depend only on the atmospheric pressure viscosity of the fluid in the contact inlet. In this chapter and the next, a polymer/steel or polymer/glass contact is referred to for convenience as a “soft contact”.

While this soft contact approach meant that it was very easy to establish a low pressure lubricated contact, it created a new problem of how to measure film thickness. This is because the main techniques to measure film thickness, optical interferometry and

capacitance, could not be directly transferred to a contact where one surface was polymeric and thus (i) not optically reflective and (ii) not electrically conducting. Two methods were therefore explored to measure hydrodynamic film thickness in soft contact. The first was to apply Hart and Hidrovo's static double dye fluorescence method [1-3] to a dynamic tribological soft ball on glass disc contact using a CETR tribometer. The second technique was to apply coatings to polymer surfaces in order to be able to use conventional optical interferometry and a PCS optical test rig with the soft contact.

During this study it emerged that the latter technique had distinct advantages over the former in terms of ease of use and accuracy, so it became the method of choice. Hence, double dye fluorescence will only be briefly described.

5.2 DOUBLE DYE FLUORESCENCE TECHNIQUE

In order to be able to investigate fluorescence based film thickness measurements on a CETR it was necessary to develop a high speed, elevated disc drive and an inverted microscope, as shown in figure 5.1.

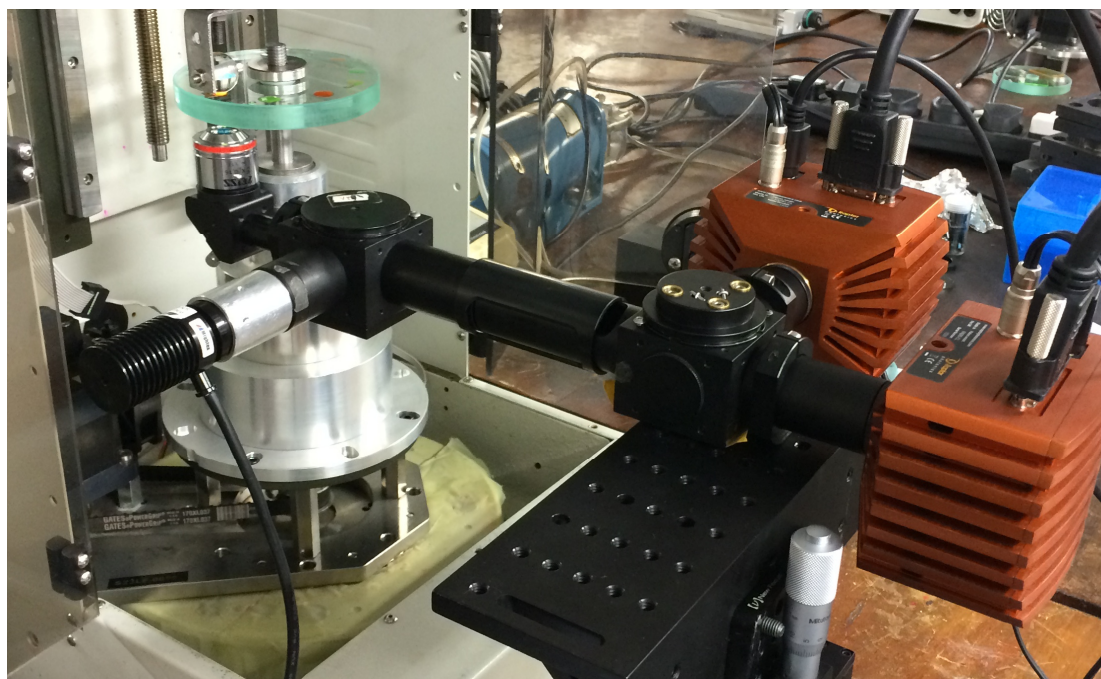


Fig. 5.1: Elevated disc drive and inverted microscope fit onto a CETR tribometer

In conventional laser induced fluorescence (LIF), a fluorescent dye is dissolved in the lubricant. This dye adsorbs light of one wavelength and emits light (fluoresces) at a longer wavelength. By measuring the intensity of the emitted light the film thickness can be estimated. However this technique has a number of practical problems that reduce its accuracy. In particular calibration is difficult while temporal and spatial variations in the intensity of the laser light source or the sensitivity of the detector lead to errors. To address some of these problems, Hart and Hidrovo developed a double dye technique that uses two dyes in solution in the test oil.

Two oil soluble dyes were initially selected for this purpose: pyrromethane 546 (PM546) and phenoxazone 9 (PH9). The absorption and emission spectra of the dyes diluted in DEHP, were measured with a spectrometer and are displayed in figure 5.2. Figure 5.3 shows the optical setup. A Mightex LED giving wavelength 490 nm is directed via a long-pass 506 nm dichroic filter towards the objective underneath the contact. A band-pass filter ensures that the excitation light source does not emit any wavelengths above the dichroic splitting wavelength. In the contact the LED excites the two dyes. The dyes emit light in all directions. About 5-10% of the light is captured by the objective and shone back into the microscope. The light emitted is of higher wavelength than the first long pass dichroic splitting wavelength, thus passing through it. A lens focuses the image into the two cameras. The two emitted spectra are split with a long-pass 546 nm dichroic into each camera. The PH9 passes through the dichroic into the first camera, while the PM546 is reflected into the second camera.

In order to eliminate parasite light from the LED and from the respective other dye, a band-pass filter between 506 nm and 546 nm is fitted to the PM546 camera and a long-pass filter above 625 nm is fitted to the PH9 camera.

Hence each dye creates an image of the contact and the two images are visualised by the two EMCCD cameras.

The PH9 dye absorption spectra overlaps the PM546 dye emission spectra. Hence, depending on how many dye molecules of each dye are present in the contact, some of the light emitted by the PM546 dye is absorbed by the PH9 and thus shines less intense

in its camera. At fixed dye concentration in the lubricant, film thickness is the only variable that varies the number of dye molecules in the contact. Consequently, the magnitude of absorption may be related to the in-situ film thickness.

After image background subtraction, by dividing the emission image of PH9 by the emission image of PM546, absorption magnitude and thus film thickness profiles may be determined across the contact.

It should be noted that the emission ratio is also dependent on filter selection.

During testing it was found that phenoxazone 9 had very limited solubility in DEHP and that its emission efficiency was quite low. Therefore it was replaced by pyrromethane 650, which has similar absorption and emission spectra to phenoxazone 9.

The advantages of the double dye technique over single dye intensity based fluorescence is that any optical discrepancies, such as reflections in the contact or dust on the filters, are cancelled out by the ratiometric image. Furthermore, significantly larger variations in film thickness may be measured with the ratiometric approach. Thus the film thickness profile outside of the contact can be measured.

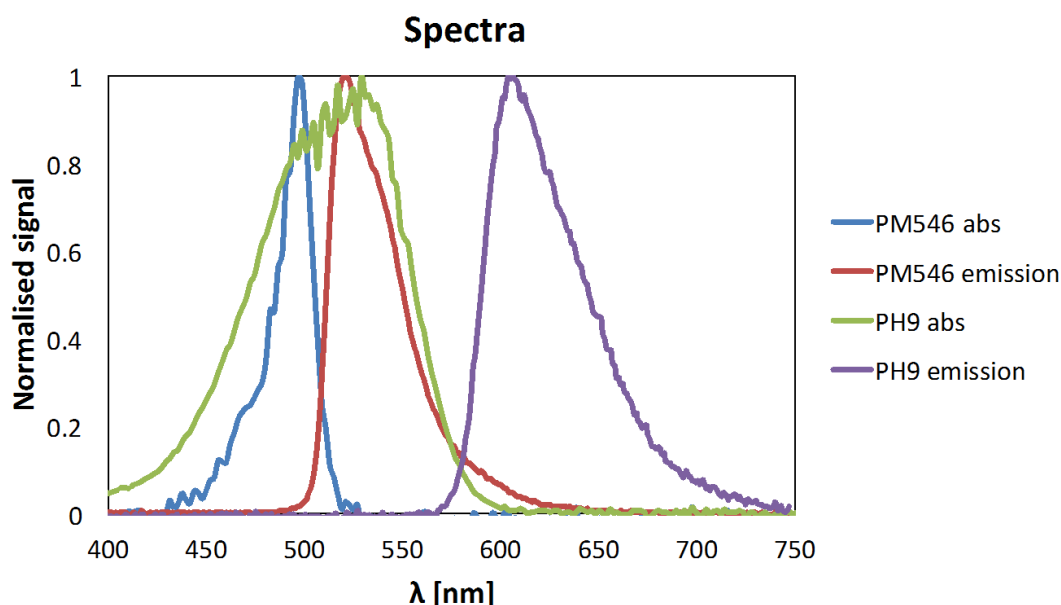


Fig. 5.2: Absorption and emission spectra of a successful double dye setup

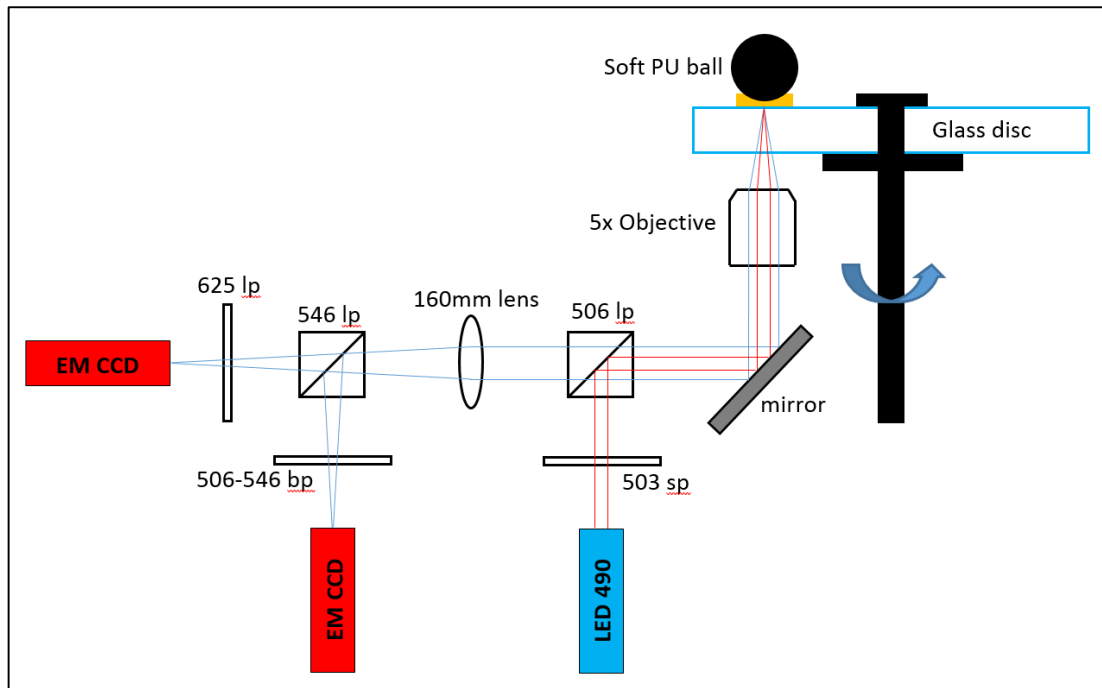


Fig. 5.3: Optical setup for double dye fluorescence

Figure 5.4 shows a fluorescent ball on disc contact.

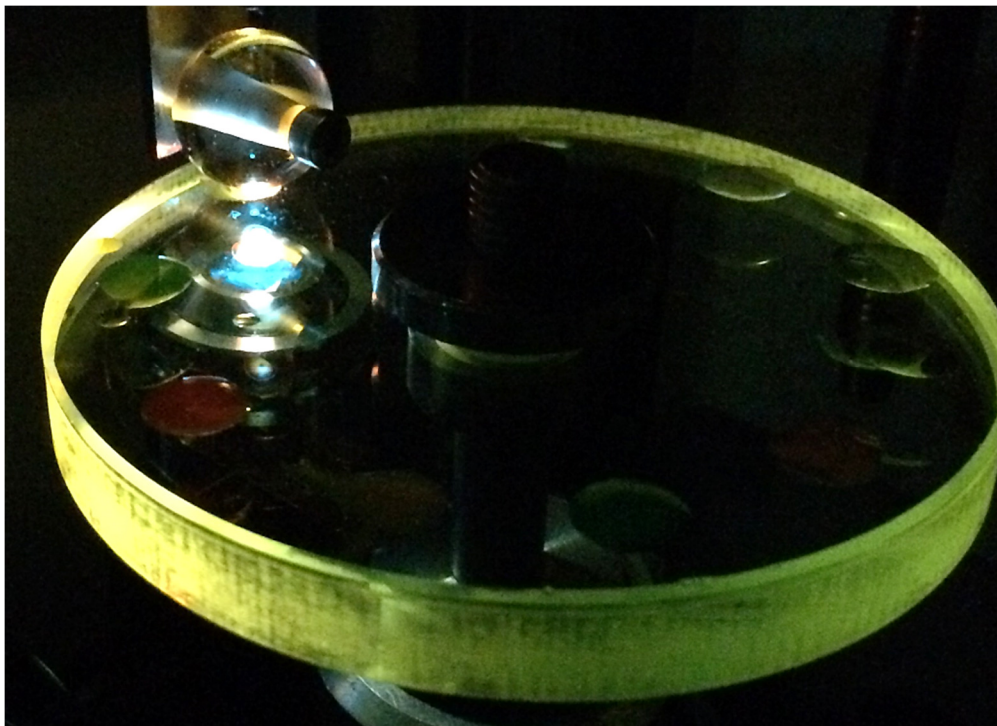


Fig. 5.4: Fluorescent ball on disc contact

Figure 5.5 shows ratiometric images of a pure sliding contact of a polyurethane hemisphere and a glass disc at 0.5 N load at room temperature. The lubricant used is 2% wt. 200k g/mol polystyrene in DEHP. As sliding speed increases, the ratiometric value in the contact increases. As a result, the film thickness increases, as expected from hydrodynamic theory.

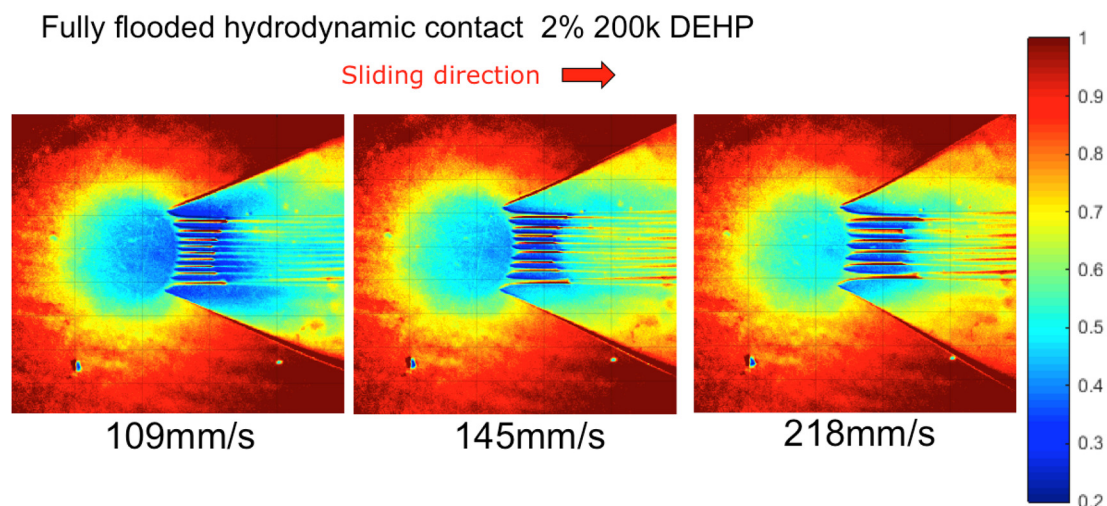


Fig. 5.5: Ratiometric images in a dynamic soft hemisphere on glass disc contact for different entrainment speeds. Scale is ratio of images

In order to convert the ratios to a film thickness, measurements were made from stationary contact and mapped against the out-of-contact separation calculated from Hertz theory. Figure 5.6 shows experimental plots of Hertz separation against measured fluorescence intensity ratio taken from outside a static contact, showing both the thin film region close to the contact edge and the thicker film region further out. Figure 5.7 shows film thickness profiles obtained using this calibration from both a static and the sliding contact images in figure 5.5.

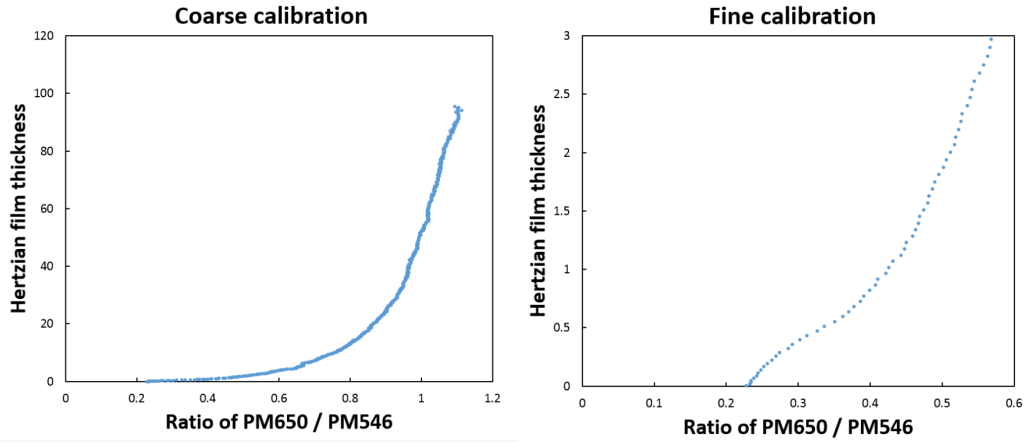


Fig. 5.6: Ratiometric calibration against film thickness, for thick and thin films

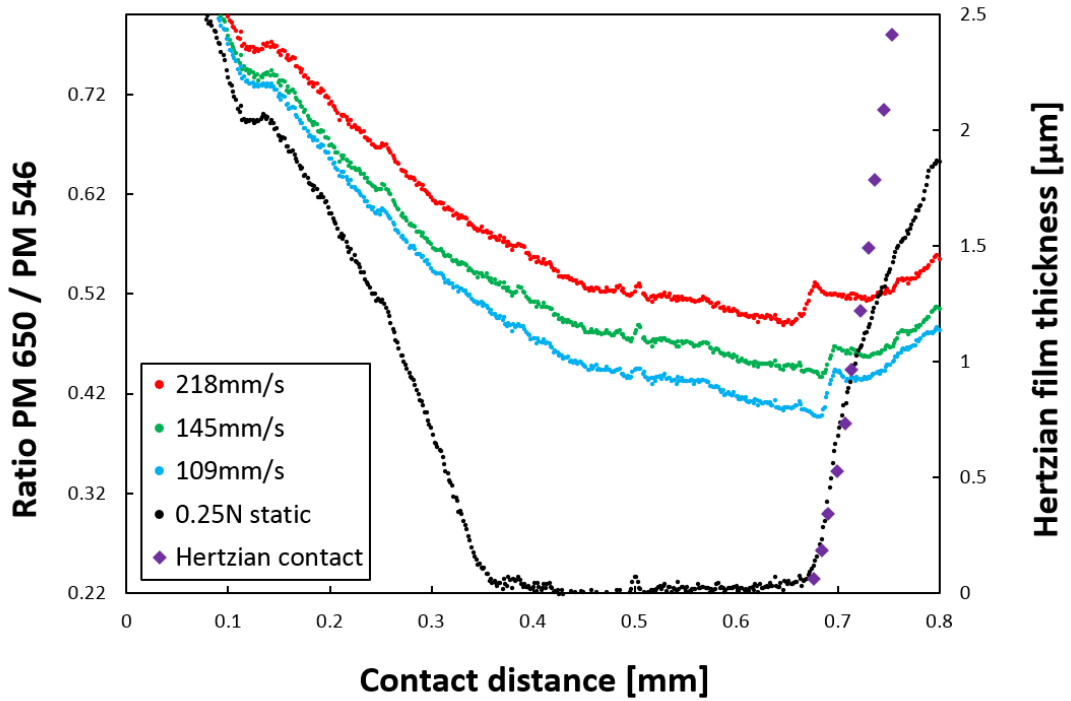


Fig. 5.7: Hertzian and dynamic ratiometric contacts

The advantage of using this optical setup on the CETR tribometer is that it is possible to obtain hydrodynamic film thickness and hydrodynamic friction measurements simultaneously and Figure 5.8 shows hydrodynamic friction measurements taken together with the images in figure 5.5 and the consequent profiles in figure 5.7.

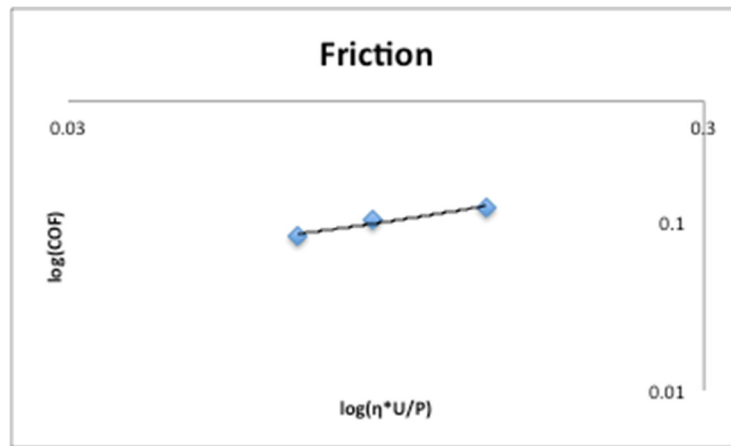


Fig. 5.8: Hydrodynamic friction in a dynamic soft hemisphere on glass disc contact for different entrainment speeds

Considerable efforts were made to develop the dual dye fluorescence method into a useful technique for the study. Because variation of working distance affected the measured intensities, an ultralow runout rotating disc platform was designed and manufactured as well as a more robust inverted microscope, as shown in figure 5.9.

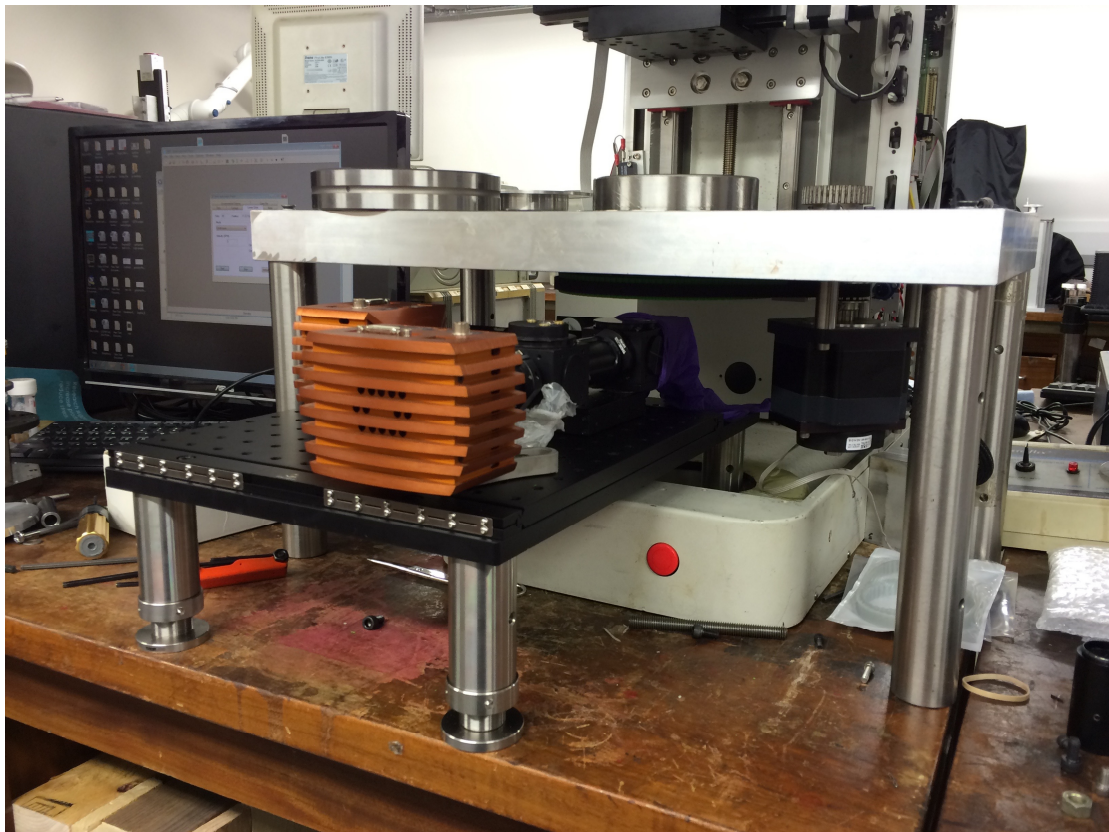


Fig. 5.9: Ultra low runout platform and robust inverted microscope.

However ultimately it was determined that the optical interference approach gave considerably more accurate film thickness measurements and this became the preferred technique for further work.

5.3 *[4]SOFT CONTACT INTERFEROMETRY TECHNIQUE**

5.3.1 INTERFEROMETRIC SETUP

In lubrication research, optical interferometry is normally used to measure EHD film thickness in a steel or tungsten carbide ball on coated glass or sapphire contact, as shown in figure 5.10. The ball is half-immersed in lubricant held in a test chamber at a controlled temperature. Ball and disc are driven by two independent motors and the motor speeds, applied load and lubricant temperature are all controlled by computer. Light is shone into the contact through the glass disc where half is reflected back from a semi-reflective coating on the underside of the disc and half travels through the lubricant film to be reflected back from the ball. The two reflected beams optically interfere and the resulting interfered light is either passed to a spectrometer to determine the wavelength of maximum constructive interference and thus the film thickness at one location in the film or is captured directly and its interference colours compared to a colour/film thickness calibration to obtain a map of film thickness. Figure 5.10 shows a captured interference image, where the inlet is on the bottom and the exit at the top of the image.

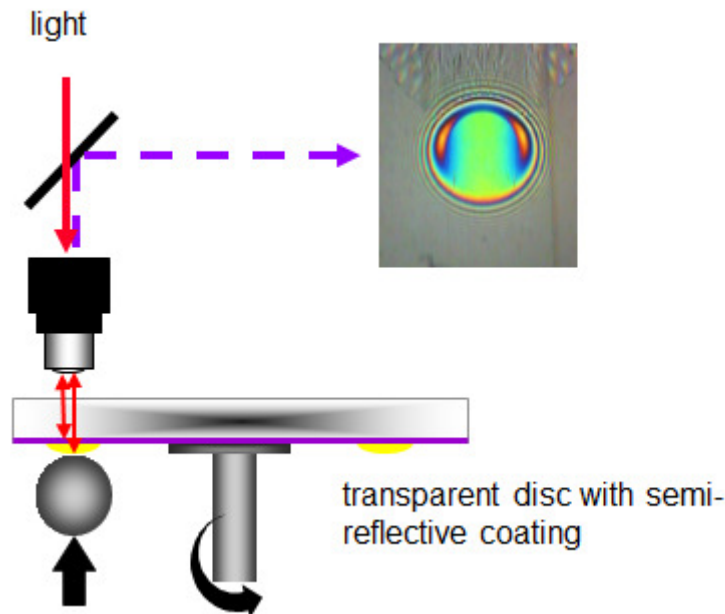


Fig. 5.10: Interferometric setup and image result

This technique requires two reflective surfaces, in figure 5.10 the ball and the coating on the underside of the disc. The problem with using this method with a soft contact is that polymers are not generally reflective and it has not proved possible in the past to apply durable semi-reflective coating to the polymer surface. Various attempts have been made to overcome this problem; polishing elastomers to make them as reflective as possible; using an indirectly aligned light source to enable interferometry with very little reflection and even applying a gold semi-reflective coating but these have not proved successful or easy to use.

In this project however it was found that reasonably durable semi-reflective chromium coatings could be applied to polymer discs to enable the set up shown in figure 5.10 to be used to study soft contact. It is not clear why this has not been successfully done in the past but it may be that attention has always focused on very compliant elastomer materials such as rubber and silicone and the very large local deformations that these undergo in contact damaged any coatings applied. In the current study the focus was on plastic polymers which are considerably less compliant and thus experience much less local deformation.

Film thickness measurements were therefore made in this study using chromium-coated polymer disc on steel ball contacts in optical interferometric test rig (PCS

Instruments, Acton, UK). This test rig is normally used with transparent disc coated with a semi-reflective coating on top of which is a silica spacer layer coating to enable very thin lubricant films to be measured. In the current study a silica spacer layer was not employed since the interest as in relatively thick lubricant films.

5.3.2 THEORETICAL EQUATIONS

Considerable numerical modelling work has been carried out to solve combinations of the Reynolds, elastic deformation and piezoviscosity equations and thus develop regression equations to predict both central and minimum film thickness in all of the four hydrodynamic regimes [5-8] shown in figure 5.11. For the circular point contact of interest to the current study, Esfahanian and Hamrock provide non-dimensional central, H_c and minimum, H_o film thickness equations [7];

$$\text{isoviscous-rigid, } H_c = H_o = 140 \quad (5.1)$$

$$\text{piezoviscous-rigid, } H_c = H_o = 5.35g_v^{0.375} \quad (5.2)$$

$$\text{isoviscous-elastic, } H_c = 5.08g_E^{0.67}, H_o = 3.28g_E^{0.67} \quad (5.3)$$

$$\text{piezoviscous-elastic } H_c = 2.55g_v^{0.53}g_E^{0.13}, H_o = 1.69g_v^{0.49}g_E^{0.17} \quad (5.4)$$

where

$$H_c = H_o = \left(\frac{h_{c/o}}{R'_x} \right) \left(\frac{\bar{W}}{\bar{U}} \right)^2 \quad (5.5)$$

$$g_v = \frac{\bar{G}\bar{W}^3}{\bar{U}^2} \quad (5.6)$$

$$g_E = \frac{\bar{W}^{8/3}}{\bar{U}^2} \quad (5.7)$$

and

$$\bar{U} = \frac{Ue\eta_0}{E'R'_x} \quad (5.8)$$

$$\bar{W} = \frac{W}{E'R_x'^2} \quad (5.9)$$

$$\bar{G} = \alpha E' \quad (5.10)$$

h is the film thickness, U the entrainment or mean rolling speed, W the applied load, η the dynamic viscosity and α the pressure viscosity coefficient of the lubricant. The reduced radius and reduced elastic modulus are defined respectively by;

$$\frac{1}{R'_x} = \frac{1}{R_{x1}} + \frac{1}{R_{x2}} \quad (5.11)$$

$$\frac{2}{E'} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \quad (5.12)$$

where R_{x1} and R_{x2} are the radii of the two solid bodies in the entrainment direction and E_1 , E_2 and ν_1 , ν_2 are the elastic moduli and Poisson's ratios of the two bodies.

The above elastic-isoviscous equations can be reduced to;

$$\frac{h_c}{R'_x} = 5.08\bar{U}^{0.66}\bar{W}^{-0.21}, \frac{h_0}{R'_x} = 3.28\bar{U}^{0.66}\bar{W}^{-0.21} \quad (5.13)$$

These equations are very similar to Hamrock and Dowson's isoviscous-elastic equations which for circular contact reduce to [9];

$$\frac{h_c}{R'_x} = 3.3\bar{U}^{0.64}\bar{W}^{-0.22}, \frac{h_0}{R'_x} = 2.8\bar{U}^{0.66}\bar{W}^{-0.21} \quad (5.14)$$

Hooke has noted that the elastic-isoviscous and elastic-piezoviscous regimes should each be divided into two regions depending upon whether the minimum film thickness occurs at the exit of the contact or in the side lobes and that for circular contacts there is a transition from the former to the latter as the pressure increases or the entrainment speed decreases [10,11]. For the elastic-isoviscous regime he provides equations to estimate the minima at both positions [10];

$$H_0(exit) = 2.83g_E^{0.7} \quad (5.15)$$

$$H_0(side) = 8.55g_E^{0.625} \quad (5.16)$$

while suggesting the central film thickness to be;

$$H_c = 3.56g_E^{0.7} \quad (5.17)$$

These are equivalent to

$$\frac{h_c(exit)}{R'_x} = 2.83\bar{U}^{0.6}\bar{W}^{-0.13} \quad (5.18)$$

$$\frac{h_c(side)}{R'_x} = 8.55\bar{U}^{0.75}\bar{W}^{-0.23} \quad (5.19)$$

$$\frac{h_c}{R'_x} = 3.56\bar{U}^{0.6}\bar{W}^{-0.13} \quad (5.20)$$

Two methods can be used to determine the regime in which a non-conforming lubricated contact will operate. One is to use maps to demarcate the various regimes

in terms of two non-dimensional variables. A second approach is simply to calculate the predicted film thickness using four equations, each applicable to a different regime. Then the equation that predicts the thickest hydrodynamic film corresponds to the regime in which the contact will operate.

Figure 5.11 shows a regime map for circular point contact derived from the minimum film thickness Eq. 5.1-4. The dashed line marks Hooke's suggested boundary between the isoviscous elastic regime where the minimum is at the exit of the contact (I-E (exit) and that where is at the sides (I-E (side)).

5.3.3 MATERIALS

Two transparent polymer discs were employed in place of the normally-used glass disc, one of polymethylmethacrylate (PMMA) and the other of polyurethane (PU). In Chapter 6 also a polycarbonate (PC) disc will be implemented. Their properties are listed in Table 5.1 and were determined by applying different loads to the ball, measuring the contact diameter and comparing it to Hertzian theory.

Table 5.1: Polymer discs studied

	Material	Thickness	Surface Roughness, Ra measured (sensitivity <10nm)	Elastic modulus	Poisson's ratio
PMMA	Polymethylmethacrylate	10 mm	< 4 nm	3.3 GPa	0.39
PU	Polyurethane	10 mm	< 4 nm	1.85 GPa	0.48
PC	Polycarbonate	10 mm	< 4 nm	2.2 GPa	0.37

Film thickness tests were carried out over the range of conditions, $U = 0.135$ m/s to 4 m/s, $W = 5, 10$ and 15 N, and slide roll ratio, $SRR = -1.5$ to 2, where SRR is defined as the ratio of sliding to mean rolling speed, $(u_D - u_B)/U$, where u_D and u_B are the surface speed of the disc and ball respectively and U is the mean rolling speed, $(u_B + u_D)/2$. All

tests described in this chapter were carried out at 40°C. For PMMA-steel, loads of 5 N, 10 N and 15 N were used, corresponded to mean Hertz pressures of 35, 45 and 51 MPa respectively, while for PU-steel the corresponding mean pressures were 27, 34 and 39 MPa. The above test conditions meant that all tests operated in the isoviscous-elastic regime within the region shown as an elongated diamond in figure 5.11.

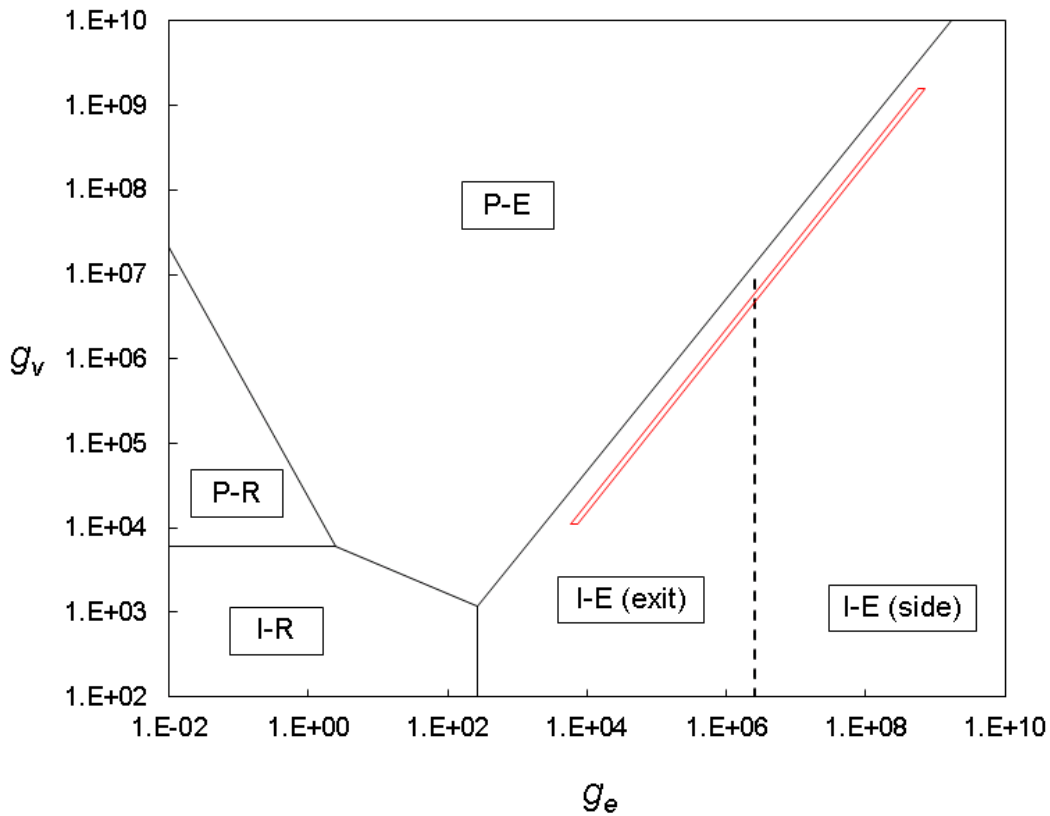


Fig. 5.11: Hydrodynamic regime map for circular point contact adapted from [12]

Normally the ball is part-immersed in lubricant. However for pure sliding with $SRR = 2$ the ball does not rotate so that it is unable to draw lubricant from the reservoir into the contact. In this case the disc surface was copiously supplied with oil at the start of a test and the test time limited to avoid possible starvation. It was not possible to test the case of $SRR = -2$ with the disc stationary since the software system for image capture required triggering from the rotating disc.

Two additive-free, hydrocarbon base fluids were used in this study, both of gas-to-liquid origin and corresponding broadly to API Group III+. Their viscometric

properties are listed in Table 5.2. Viscosities were measured using an Anton Paar SVM 3000 Stabinger viscometer. The effective pressure viscosity values, α listed in Table 5.2, which were used solely to plot the range of study in figure 5.11, were determined by comparing EHD film thickness measured by optical interferometry with the EHD film thickness formed by a reference oil of known α^* [7]. Refractive indices of the lubricants, required to convert optical to spatial film thickness, were measured using an Abbe refractometer.

Table 5.2: Viscosities of test lubricants

	Viscosity 40°C cP	Viscosity 100°C cP	Density 40°C g/cm ³	Density 100°C g/cm ³	Effective α -value 40°C GPa ⁻¹	Effective α -value 100°C GPa ⁻¹
GTL4	14.77	3.08	0.80	0.76	14	12
GTL8	35.86	5.93	0.81	0.78	15	12

5.3.4 OPTICAL INTERFEROMETRY METHOD

The PCS optical interference rig normally uses a white light source, which is suitable to use with a spectrometer to measure very thin films. However it is less well-suited to measure thick films since the continuous light spectrum leads to a blurring of interference fringes above the fourth interference order. Instead a white LED light source was used showing two marked peaks, one at around 460 nm, the other at 560 nm. The relative sharpness of the peaks gave rise to good fringe visibility in the three channels (red, green and blue) and this meant that films up to 1.5 microns thick could be measured, although the maximum film thickness used in this study was only 1.2 microns.

In order to characterise the light source a static contact was initially produced between a chromium-coated glass disk and a steel ball and the contact flooded with lubricant. The resulting interference fringes were scanned radially and fringe intensities in the red, green and blue channels were plotted against the gap calculated using Hertz theory [13]. As described in Guegan *et al.* [14] the intensities were then normalised by the

neighbouring minimum and maximum value of the intensity for each branch, so as to obtain values between -1 and 1.

This process produces sinusoidal curves whose periods correspond to the average wavelength of the light source modulated by the response of the camera. The shifts of these curves give the phase shift resulting from reflection from the chromium layer. Analysis of the fringes gave the properties of the light source and the optical system shown in Table 5.3.

Table 5.3: Wavelengths of RGB optical channels and phase shift of coated glass disc

λ_{Red}	λ_{Green}	λ_{Blue}	ϕ
590 nm	520 nm	470 nm	0.15

According to optical theory, the period of the fringes against film thickness for a light source with wavelength λ' , *i.e.* the difference in film thickness between two consecutive peaks or troughs T' is:

$$T' = \frac{\lambda'}{2n'} \quad (5.21)$$

where n' is the refractive index of the oil. In these tests, the refractive index was measured as 1.450 for the GTL4 and 1.455 for GTL8 at 40°C. This difference was too small to have any significant impact on the periods, so the same mean value was used for both oils to give $T_R = 203$ nm, $T_G = 179$ nm, $T_B = 165$ nm.

A similar procedure was then carried out in static contacts formed between the two polymer discs and the steel ball. Using the wavelengths calculated above, this resulted a non-zero film thickness in the contact area due to a different phase shift and from this a revised phase shift value could be determined. This was done for the three channel profiles independently, but the phase shifts obtained from all were identical, at a value of 0.10 for both polymers. This approach avoided making the assumption that the static polymer-steel contacts were Hertzian, although in practice their profiles were found to be very close to this.

One problem in optical interferometry, especially when studying thick lubricant films, is to determine the correct interference order. This can be done by counting the order change while gradually increasing the entrainment speed and thus the film thickness from zero. In the current study this was combined with a method for directly determining order, as described below.

After each polymer-steel test, the interference images (interferograms) were post-processed individually. An image contains three colour planes, one for each channel. As shown below in figure 5.12, a rectangular strip was selected that traversed the contact and for each channel the intensities of the pixels across the thickness of this strip were averaged to reduce noise. Typically 15 pixels were averaged, few enough to ensure the thickness was essentially constant in the direction averaged. This gave R G and B intensity profiles across the contact as shown in figure 5.13(left). As explained above and shown in figure 5.13(right) the three intensity curves were then normalised between -1 and 1.

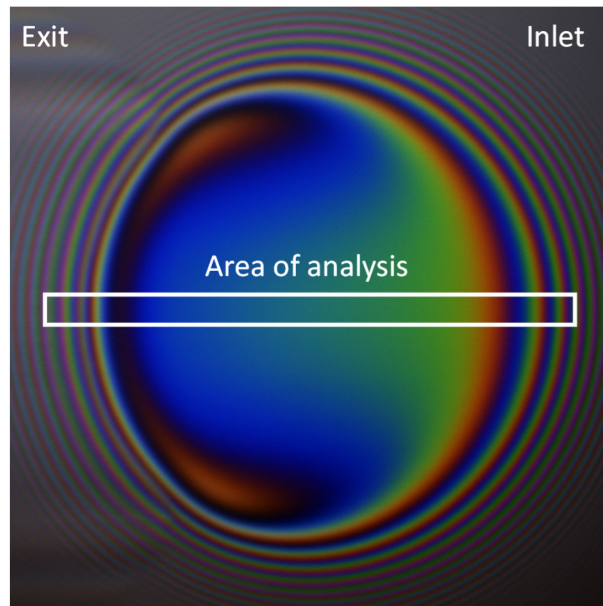


Fig. 5.12: Interferogram showing the rectangular region where the film profile is calculated (PMMA, GTL8, $W = 5$ N, $U = 1.6$ m/s, $SRR = 0$)

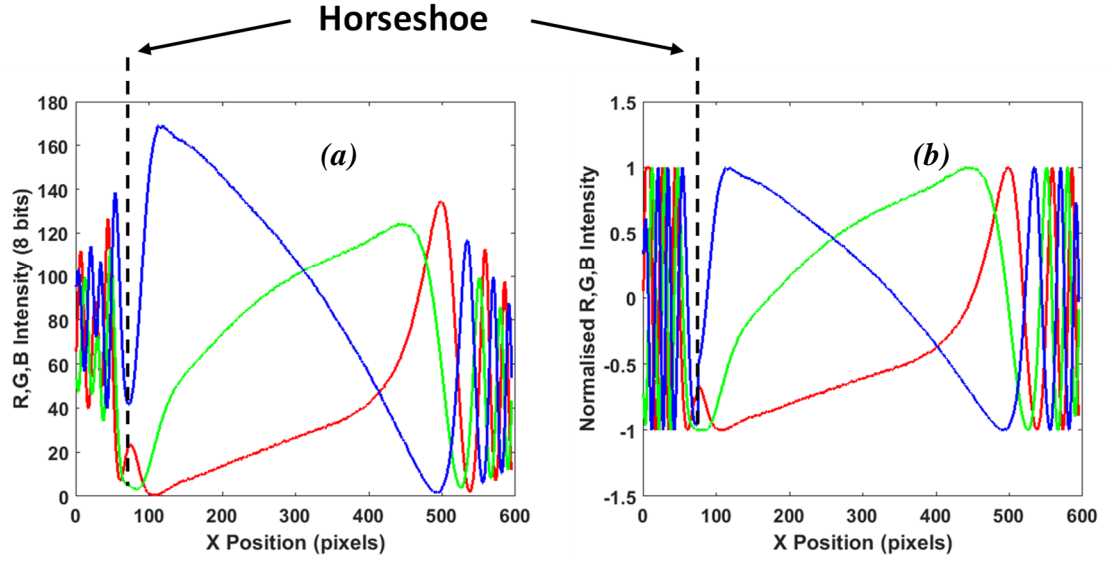


Fig. 5.13: Measured intensity along the contact (left) and normalised intensity (right); the position of the horseshoe minimum is also shown

As noted above, the difference in film thickness between two peaks or troughs depends on the wavelength of the light source. Assuming the film thickness evolves monotonically (positively or negatively), the fringes can then be counted and the difference in film thickness between two points calculated. For the points that do not lie at a minimum or maximum of intensity the film thickness was calculated based on the thickness varying with the arcsine of the normalised intensity. A more detailed mathematical treatment of this process can be found in Guegan *et al.* [14].

For each image, the minimum of the horseshoe (at the rear or the side of the contact depending on the direction of the strip being analysed) was identified manually, its position usually being obvious as it corresponds to a cusp on the curve. This enabled a profile to be separated into two parts in which the film evolves monotonically. In figure 5.13 (right), from position $x = 0$ to the minimum of the horseshoe the film decreases, after which it increases. Using this assumption, film thickness profiles can be calculated independently for each channel based on assuming the order of interference at the horseshoe minimum. However in figure 5.14 it can be seen that if an incorrect order is picked the different profiles do not match. Thus the correct order can be determined as that which gives a good match for the thicknesses calculated from the

three colour channels, as shown in figure 5.15(left). The final profile was then taken to be the average of these three, as shown in figure 5.15 (right).

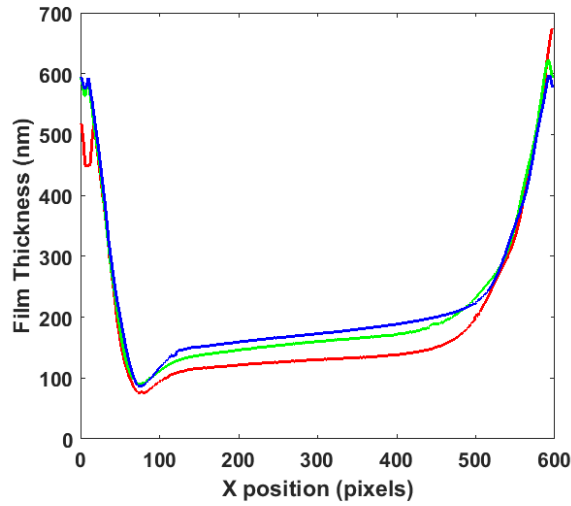


Fig. 5.14: Film thickness profiles obtained from figure 5.13 (right) using an arbitrary interference order

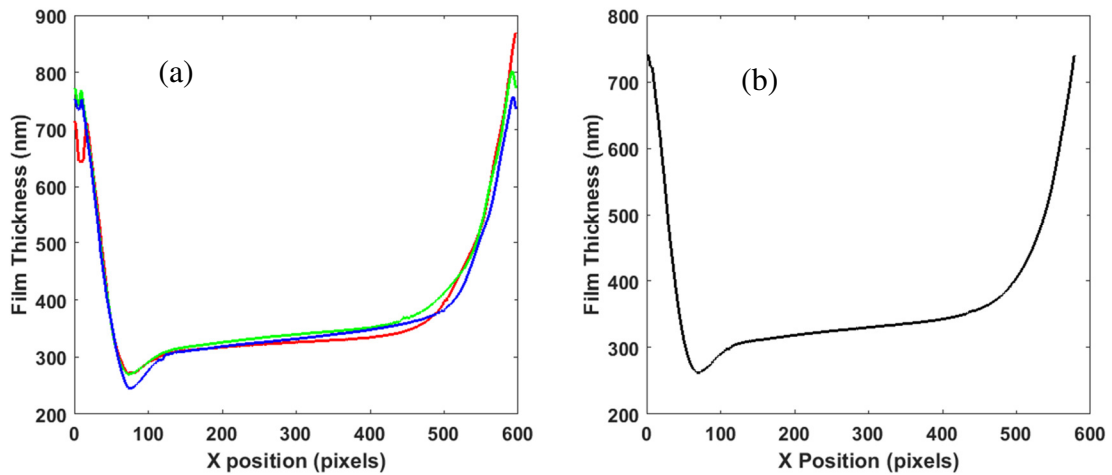


Fig. 5.15: Matching profiles for the three colour channels (left); Average profile (right)

From these profiles it was quite straightforward to determine the minimum film thickness at the exit of the contact (and for transverse profiles the minimum at the side lobes). Determination of the central film thickness was more problematic due to difficulty in identifying the contact centre precisely and also because the film thickness varied considerably across the contact at high entrainment speeds. The centre position was estimated by aligning a square over the image so the centres of the sides of the

square formed tangents to matching fringes on either side of the contact. The contact centre was then taken to be the centre of this square and the central film thickness was calculated as the average film thickness over an area corresponding to one tenth of the contact size around this central point.

An extensive study of this technique was made using several base oils and cleaning methods. These indicated an error margin of less than $\pm 0.5\%$.

5.3.5 FILM THICKNESS RESULTS

Figure 5.16 shows a series of images for a PMMA disc on steel ball lubricated by GTL8 at $SRR = 0$ and a load of 10 N. In all cases the inlet is at the bottom of the image and the exit at the top. It can be seen that the use of a chromium semi-reflective layer gives high quality interference images, similar to those obtained using a steel-on-glass disc contact as described by Foord *et al.* [15,16]. All images show the characteristic horseshoe at the rear and sides of the contact and in all of these images the absolute minimum film thickness occurs in the side-lobes.

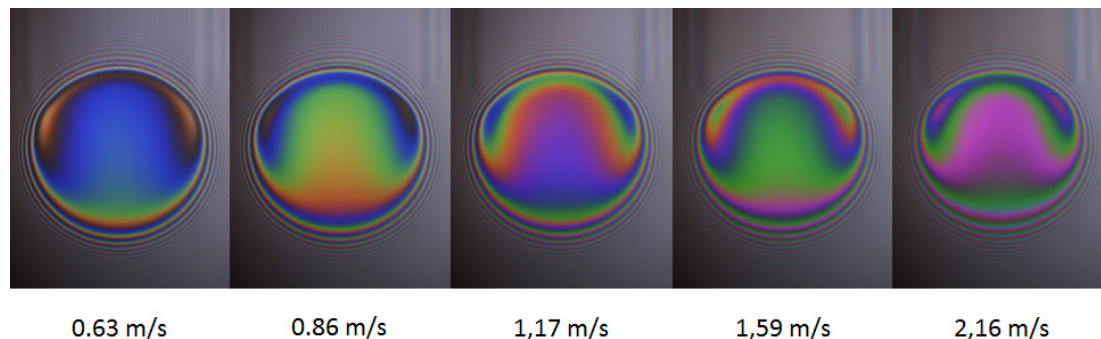


Fig. 5.16: Interferograms of the contact of PMMA disc/steel ball lubricated with GTL8 at 10N load and $SRR = 0$

Analysis of the above images together with those at other entrainment speeds gives the profiles across the centreline from inlet to exit shown in figure 5.17. The inlet is on the right of these profiles. At low speeds the central region is almost flat, similar to piezoviscous-elastic contacts, but as the speed increases a wedge-shaped film is developed. It should be noted that the thickness values in the exit beyond the minimum are not reliable because of film cavitation.

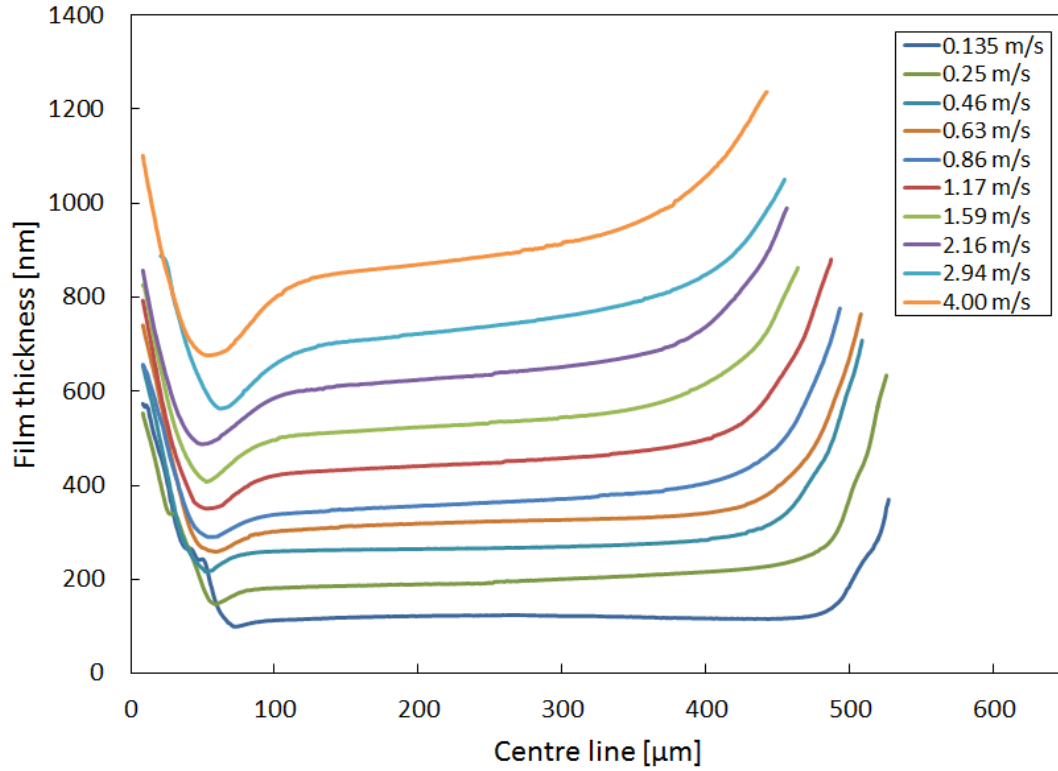


Fig. 5.17: Influence of entrainment speed on centreline film thickness profiles for PMMA disc and GTL8 at 10 N load and $SRR = 0$ (inlet on right)

Figure 5.18 shows plots of $\log(h_c)$ versus $\log(U)$ for all polymer and viscosity combinations at 10 N load and $SRR = 0$. All give straight line plots with gradients in the range 0.51 to 0.56. Minimum film thickness values in the exit (along the centreline) also gave straight line plots of similar gradient.

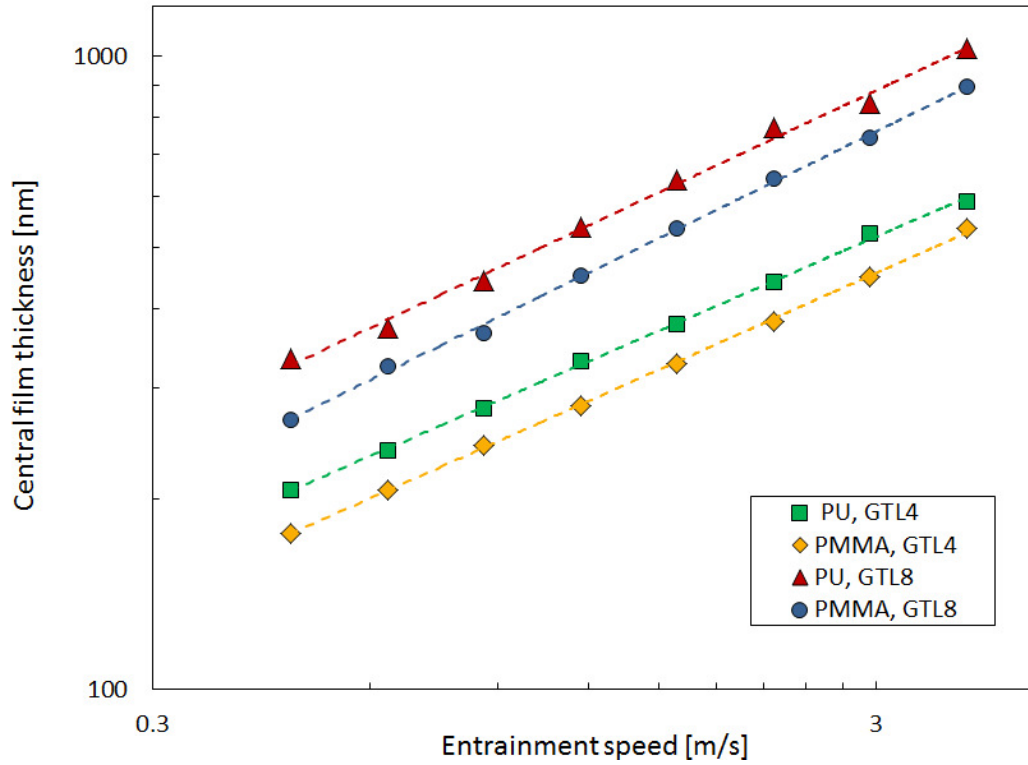


Fig. 5.18: Log(central film thickness) versus log(entrainment speed) for all four polymer/base oil combinations at 10 N load and SRR = 0

To confirm the validity of the RGB film thickness method used, central film thickness measurements were also made using the ultrathin film interferometric (UTFI) approach normally employed with the PCS Instruments optical test apparatus. This is based on spectrometric analysis of the emitted light to determine the wavelength of maximum constructive interference and thus the film thickness. This method's error limits are stated to be ± 5 nm [17] Figure 5.19 compares the measurements obtained using the two methods and shows very close agreement between them.

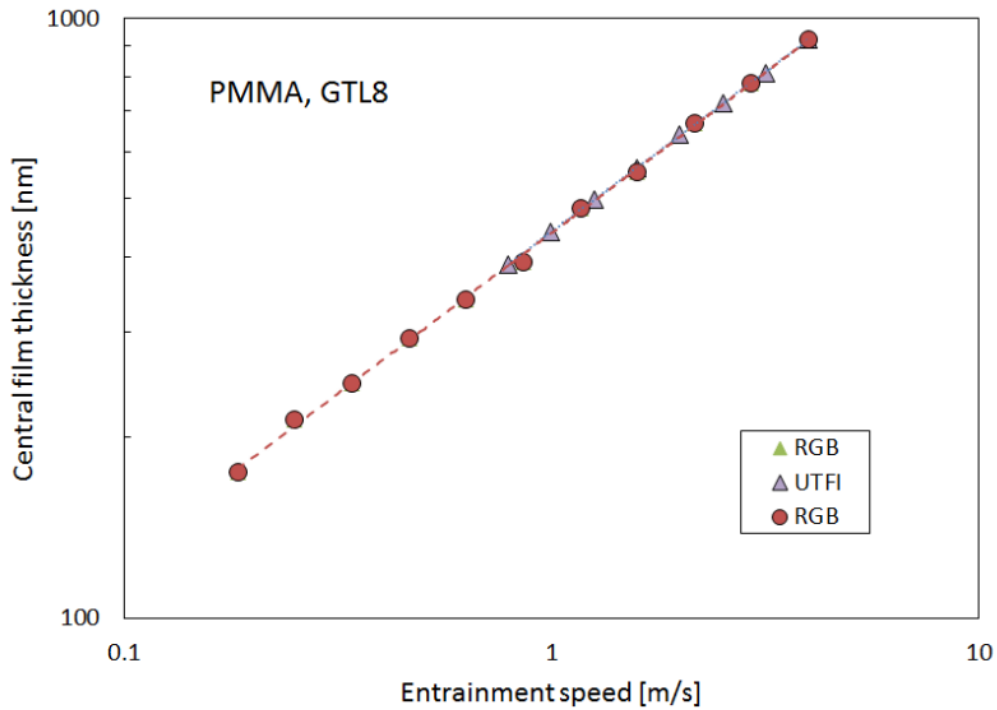


Fig. 5.19: Comparison of central film thickness measured using RGB and the UTFI methods

Figure 5.20 shows interferograms for PMMA with GTL8 at a fixed entrainment speed of 1.59 m/s and three different applied loads. The size of the contact increases rapidly with applied load but the central and exit minimum film thickness change relatively little. Profiles across the centreline from these images are shown in figure 5.21, while figure 5.22 which shows central film thickness plotted against entrainment speed for PMMA with GTL8 at the three loads.

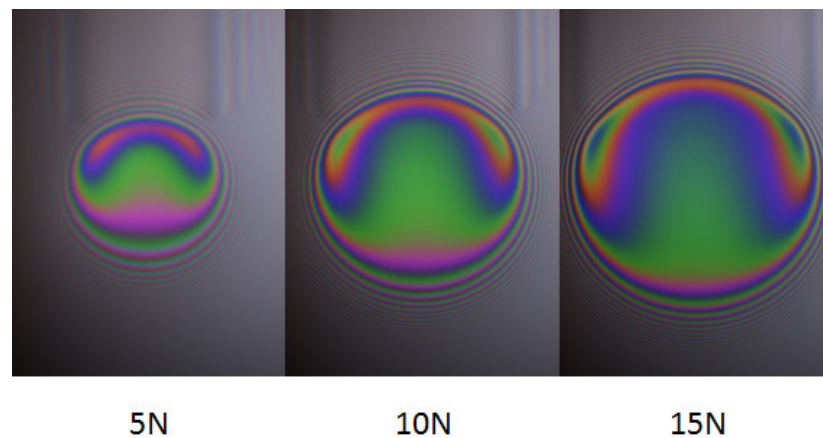


Fig. 5.20: Interferograms of the contact of PMMA disc/steel ball lubricated with GTL8 at 1.59 m/s and three different loads. SRR = 0

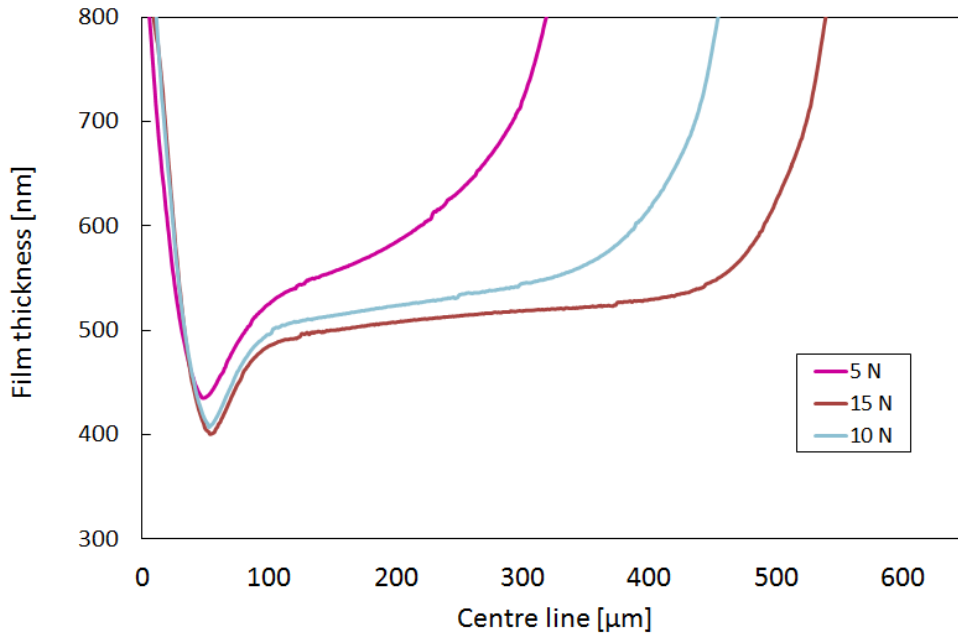


Fig. 5.21: Influence of load on centreline film thickness profiles for PMMA disc and GTL8 at entrainment speed 1.59 m/s and SRR = 0 (inlet on right)

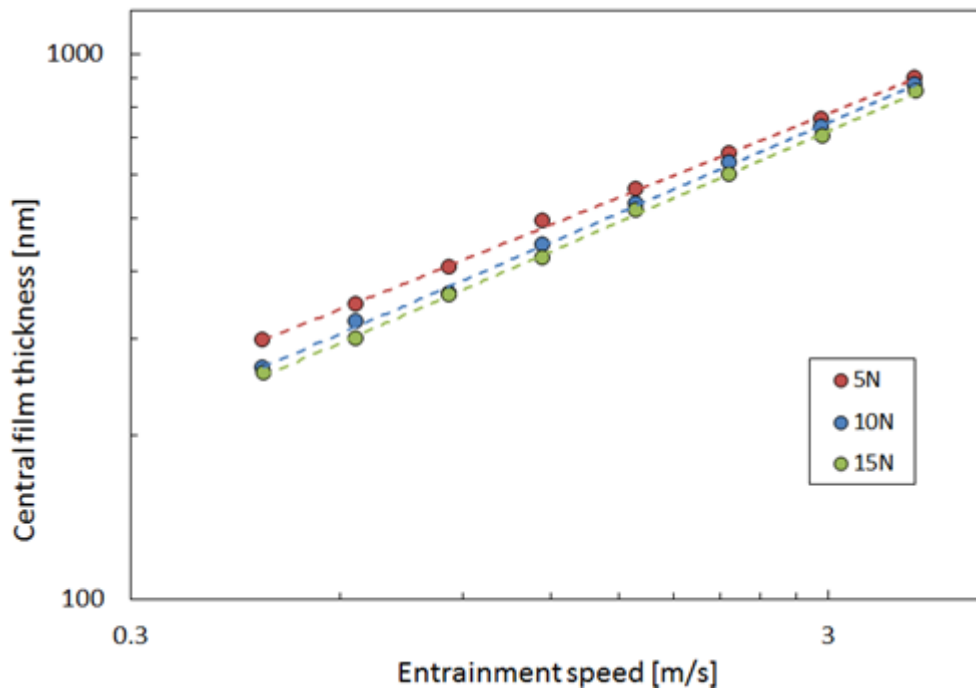


Fig. 5.22: Influence of applied load on log(central film thickness) versus log(entrainment speed) for PMMA and GTL8 at SRR = 0

All of the above results were from nominally pure rolling conditions ($SRR = 0$). Figure 5.23 shows the influence of slide-roll ratio on central film thickness for PMMA at

various entrainment speeds. In general, fluid entrainment and thus film thickness should depend only on entrainment speed and not on sliding speed and this is shown in figure 5.23 over most of the *SRR* range. The exception is at high *SRR*s, when shear heating can result in heating of the surfaces in the contact inlet leading to a reduced lubricant viscosity in the inlet and thus to a thinner film. For piezoviscous-elastic contacts this starts to be significant at *SRR* > 50% [18] but for the isoviscous-elastic contacts in this study, film thickness remains almost constant over most of the range of *SRR*. This is because much less heat is generated in these low pressure contacts, where there is negligible piezoviscous effect and so lower friction than in high pressure EHD contacts. A significant drop in film thickness is, however, seen at *SRR* = 200%. At this *SRR* the steel ball is stationary, so heat entering the ball surface within the contact is not convected towards the contact exit by rotation of the ball. This may result in an increase in ball surface temperature in the inlet but alternatively may be an effect of starvation due to inadequate lubricant supply.

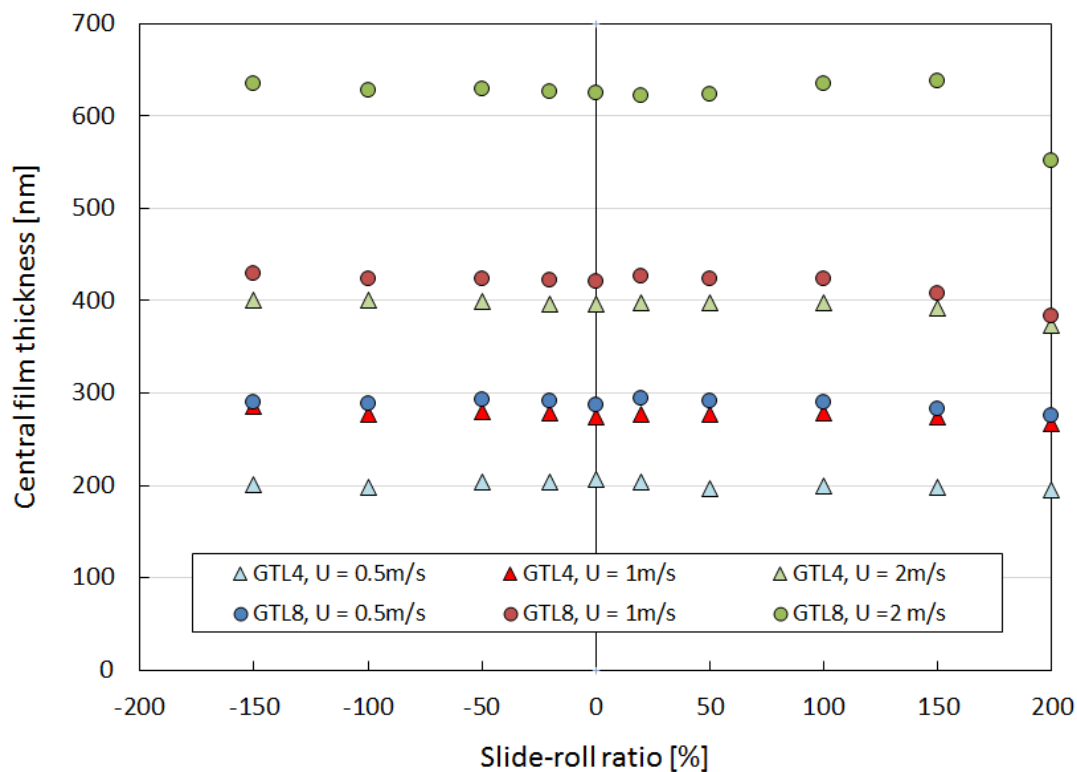


Fig. 5.23: Influence of slide-roll ratio on central film thickness for PMMA tests at $W = 10$ N.

5.3.6 DISCUSSION

Classical optical interferometry is traditionally applied to measure film thickness in piezoviscous-elastic EHL contacts. This work shows that by applying semi-reflective chromium coatings to the underside of the transparent polymer discs it can be equally well used to measure film thicknesses in the isoviscous-elastic contacts formed between polymer discs and steel balls using a commercial optical interferometry test apparatus. These coatings are quite robust and survive rolling-sliding and even pure sliding conditions so long as full film lubrication conditions are maintained. Films can be measured and mapped from ~100nm up to thicknesses in excess of one micron. A novel method of determining the order of the interference fringes has been developed based on matching calculations from the red, green and blue channels.

In this study it was found that both the central and minimum film thickness varied with entrainment speed to a power between 0.52 and 0.56. This is less than predicted by previous theoretical studies which, as indicated in Eq. 5.13, 5.14, 5.18 and 5.20 suggest a power of 0.6 to 0.66. This is illustrated in figure 5.24 where it can be seen that Dowson & Hamrock [19], Esfahanian & Hamrock [7] and Hooke [20] all predict thinner films at low speed than measured in this study.

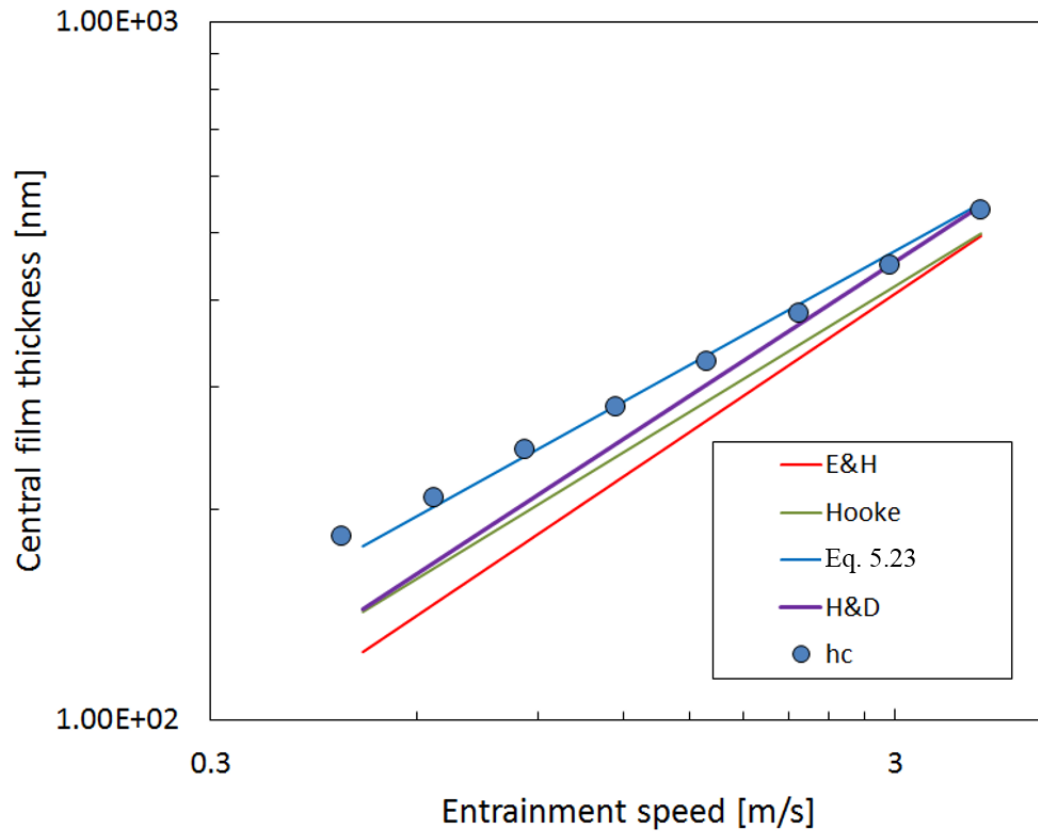


Fig. 5.24: Comparison of experimental results with measured central film thickness; PMMA, GTL4, SRR = 0

Figure 5.25 shows that all combinations of load, lubricant viscosity and elastic modulus give essentially the same central film thickness *versus* entrainment speed response. The solid lines are predictions using Eq. 5.23.

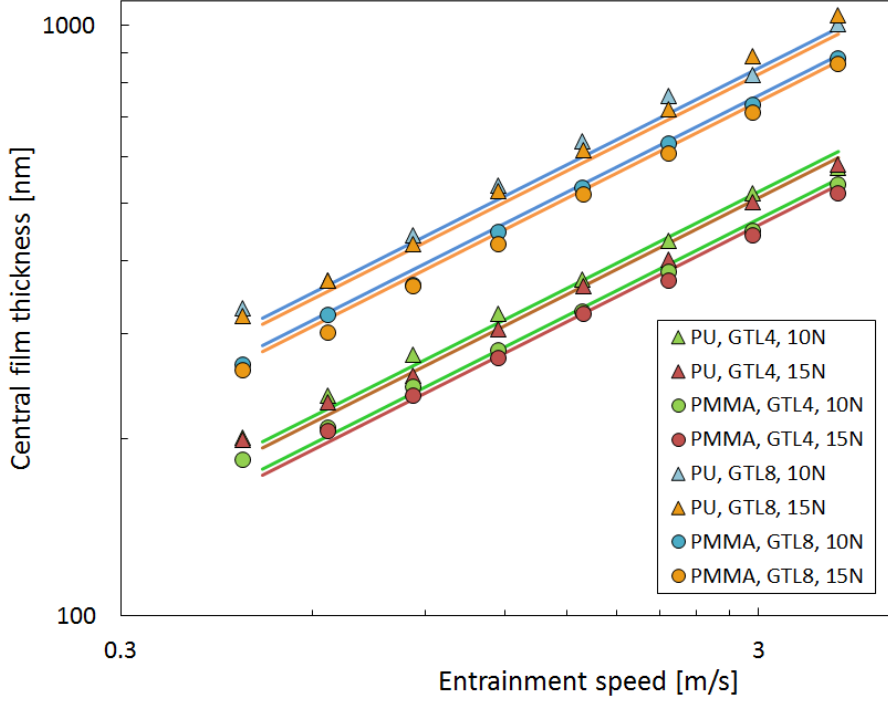


Fig. 5.25: Central film thickness versus entrainment speed for various load, viscosity and elastic modulus combinations

In soft EHL film thickness equations, film thickness is often related to a non-dimensional elasticity parameter g_E defined by Eq. 5.7.

Thus Esfahanian and Hamrock suggest an equation for central film thickness, h_c ;

$$H_c = \left(\frac{h_c}{R'_x} \right) \left(\frac{\bar{W}}{\bar{U}} \right)^2 = 5.08 g_E^{0.67} \quad (5.22)$$

By combining all of the central film thickness versus entrainment speed plots, the best fit was found to occur with a speed exponent of 0.55, *i.e.* $h_c \propto U^{0.55}$. Based on the definition of the elasticity parameter g_E given above this implies a g_E exponent of 0.725 and a load exponent of -0.067. As shown in figure 5.26, using these exponents it was found that the best fit to all of the measured central film thickness data was given by

$$H_c = \left(\frac{h_c}{R'_x} \right) \left(\frac{\bar{W}}{\bar{U}} \right)^2 = 2.7 g_E^{0.725} \quad (5.23)$$

Figure 5.27 shows that a very similar relation exists for $h_0(exit)$ except that the constant is now 2.1, i.e.

$$H_0(exit) = \left(\frac{h_0(exit)}{R'_x} \right) \left(\frac{\bar{W}}{\bar{U}} \right)^2 = 2.1 g_E^{0.725} \quad (5.24)$$

The g_E exponents in these equations are somewhat greater than those given in Eq. 5.3-17, which were determined from regression fits of computed film thicknesses.

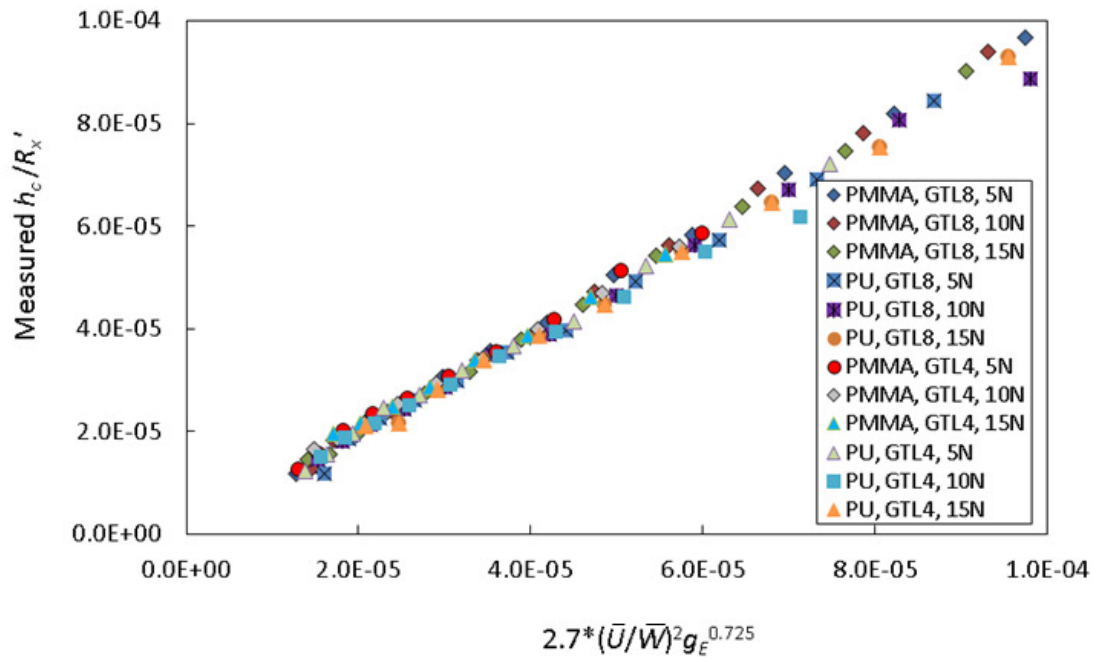


Fig. 5.26: Plot showing that all measured data fits equation $H_c = 2.7 g_E^{0.725}$

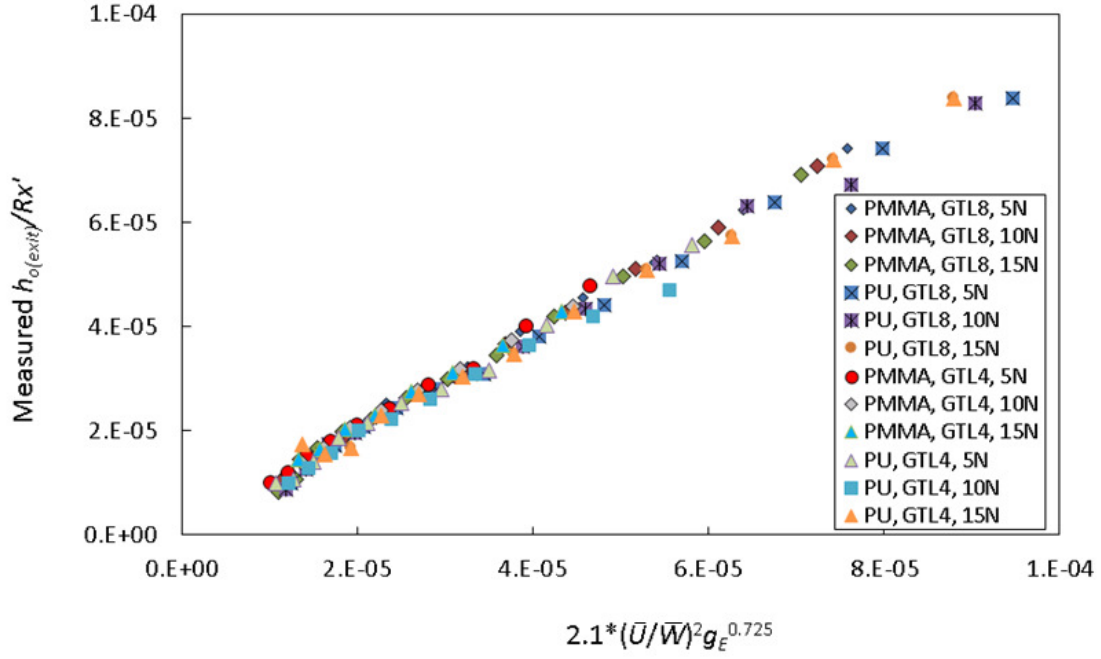


Fig. 5.27: Plot showing that all measured data fits equation $h_o(\text{exit}) = 2.1g_{\epsilon}^{0.725}$

One interesting observation in this study was that minimum film thickness was sometimes at the side lobes and sometimes on the midline at the exit. Hooke has suggested that the absolute minimum film thickness moves from the side lobes to the exit of the contact as the entrainment speed increases or the load decreases [20]. For most of the conditions tested in this study the minimum was at the side lobes but for tests at the lowest load a transition was observed with increasing entrainment speed. This is shown in figure 5.28 where it can be seen that the minimum is at the sides of the contact at low speeds but the moves to the exit as the speed is raised. A similar transition can also be seen in figure 5.20 as the load is decreased.

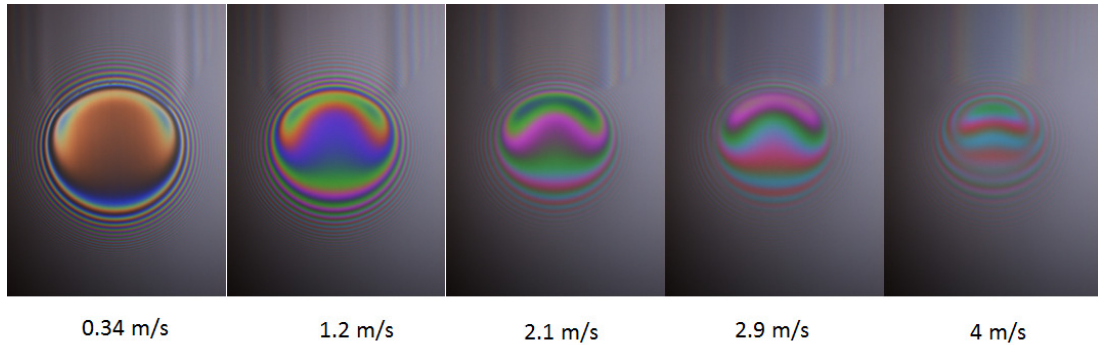


Fig. 5.28: Change in minimum film thickness position with entrainment speed, PMMA, GTL8, $W = 5\text{N}$, $\text{SRR} = 0$

The minimum film thicknesses at the exit and side lobes from figure 5.28 are plotted against entrainment speed in figure 5.29 for PMMA, GTL8 and 5 N load. The transition of the absolute minimum from the side lobes to the rear of the contact occurs at $U = 3$ m/s and $h_{min} = 595$ nm. This does not agree with the location of the transition proposed by Hooke, which he suggested should occur at $g_E = 2.6 \times 10^6$. Based on these measured results it should occur when g_E is of order 10^4 , which would just intercept the tested region in figure 5.11.

The side lobe minimum film thickness data obtained in this study was fitted to g_E . This gave a fit of similar quality to those in figures 5.26 and 5.27 and the fitted equation was;

$$H_0(side) = \left(\frac{h_0(side)}{R'_x} \right) \left(\frac{\bar{W}}{\bar{U}} \right)^2 = 2.9 g_E^{0.69} \quad (5.25)$$

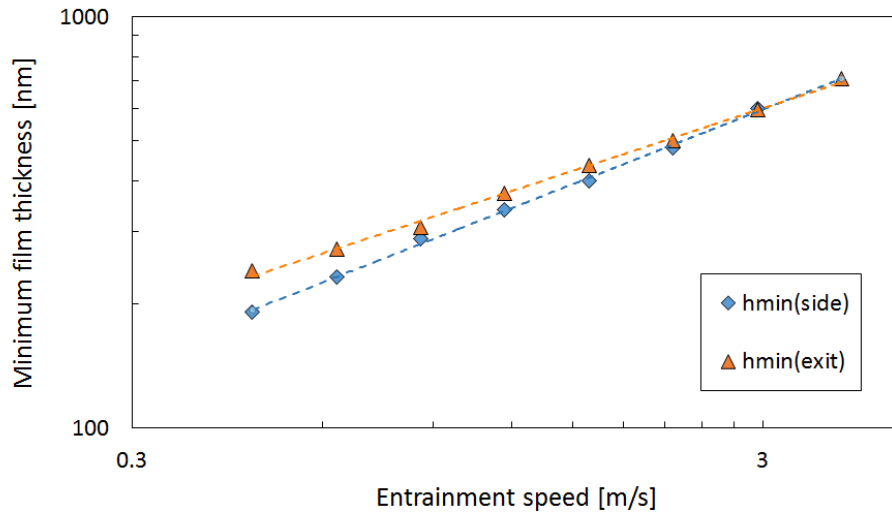


Fig. 5.29: Variation of exit and side lobe minimum film thickness with entrainment speed for PMMA, GTL8, 5N and SRR = 0

It is of interest to compare the finding of the current study using base oils with previous work on soft EHL film thickness, although unfortunately there is very little of the latter. Myant *et al.* used oblique angle interferometry to measure film thickness in a pure sliding, uncoated PDMS on glass contact [21]. This showed the formation of similar

film shapes to those in the current study, with a wedged film at high speeds and a much flatter film at low speeds. However, Myant *et al.* measured film thicknesses less than half those predicted by Dowson and Hamrock and of our experimental measurements as summarised in Eq. 5.23 above. The origins of this discrepancy are not clear. Dowson and Hamrock's equation was derived from soft EHL solutions over the range of $5 \times 10^{-9} \leq \bar{U} \leq 5 \times 10^{-8}$ and $2 \times 10^{-4} \leq \bar{W} \leq 2 \times 10^{-3}$ [22]. Myant *et al.*'s experiments were under the conditions of order $\bar{U} = 10^{-8}$ and $\bar{W} = 2 \times 10^{-4}$ while in this paper, due to the higher elastic modulus polymer employed, mid-range conditions were $\bar{U} = 2 \times 10^{-9}$ and $\bar{W} = 5 \times 10^{-5}$. The discrepancy is thus not likely to originate from the use of different ranges of test conditions.

5.3.7 A NOTE ON EXPERIMENTAL LIMITATIONS OF THE TECHNIQUE

Over time, when running a soft ball on disc contact in pure rolling, very small amounts of coating are removed. The phenomenon is amplified when the load is increased, i.e. contact pressure and when the slide to roll ratio is increased. The combination of surface deformation, surface deformation rate and hydrodynamic friction are concluded to cause the removal of the chromium layer.

By increasing the exposure time of the camera, the phenomenon is invisible in the pictures to be analysed for film thickness calculations. Figure 6.13 in the following chapter (Chapter 6) shows pictures where the chromium layer was significantly removed due to the very high slide to roll ratios. It should be noted that the different slide to roll ratios in figure 6.13 were run on the same but initially fresh track starting with the most severe case.

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6 Novel method to measure hydrodynamic friction

This chapter describes the development of a novel technique to measure hydrodynamic friction. A mini traction machine is used with a steel on plastic, lubricated contact. Friction trends are as expected from theory: however when comparing results to theory a factor of difference of the overall friction value is obtained. Numerous possible reasons are explored by experiment and by theoretical calculation. Many are dismissed and some are found to contribute. The discrepancy appears dependent on a combination of known and unknown factors, leading to the conclusion that friction experiments should be limited to only a few testing conditions for which the discrepancy reduces to one single constant factor.

6.1 MEASURING AND PREDICTING HYDRODYNAMIC FRICTION

To complement the soft EHL-based, polymer-steel film thickness method described in the previous chapter, hydrodynamic friction measurements from similar contacts were required. The PCS Instruments optical rig has the facility to measure friction from the ball shaft and in principle this could have been used to measure friction simultaneously or in parallel with film thickness measurements. Unfortunately the friction coefficient values expected from soft EHL are very low, of order 0.001 to 0.005 and such low friction values cannot be measured reliably in the optical rig. Also in the optical rig the ball shaft is horizontal which introduces spin into the contact. In soft EHL the contact diameter is large and this spin becomes substantial.

It was therefore decided to use the mini-traction machine (MTM) in a steel ball/polymer disc configuration, replacing the normally-used steel discs by polymer discs of the identical materials used in film thickness measurements. The MTM is custom-built to measure friction and can do this accurately over a wide range of contact

conditions of speed, load and temperature. The normal MTM steel discs are 6 mm thick and 48 mm in diameter, so disc of similar dimensions are required.

MTM polymer discs were produced from a single batch of PMMA material. As a first manufacturing technique, the discs were laser-cut from a flat 6 mm thick sheet of PMMA. This was effective but time-consuming since four out of five discs suffered surface damage from the melting polymer during the laser-cut and had to be discarded. It was also found that the successful discs cracked when tested in a fully lubricated MTM. The cracks initiated from the edge of the disc cut by the laser. It was however possible to avoid the cracking by sanding off these edges.

Subsequently, manual production of MTM discs using band saws, drills and mills proved more effective to produce useful discs.

The MTM loads a steel ball against the polymer disc as shown in figure 6.1. The rotational speed of both disc and ball may be controlled independently and in each direction.



Fig. 6.1: PMMA disc, steel ball MTM test implementing a very thick oil

Figure 6.2 displays a typical traction curve obtained by this method using the Newtonian oil DEHP and a load of 10 N. Unlike usual MTM traction curves implementing two steel surfaces, in a soft lubricated contact friction increases linearly with slide to roll ratio indicating Newtonian behaviour over the whole slide roll ratio range.

Increasing entrainment speed results in an increase in friction. This is because the SRR is the ratio of sliding speed to entrainment speed so that at a given SRR the sliding speed increases linearly with entrainment speed. So long as film thickness increases less than linearly with entrainment speed this means that strain rate increases with entrainment speed at a given SRR.

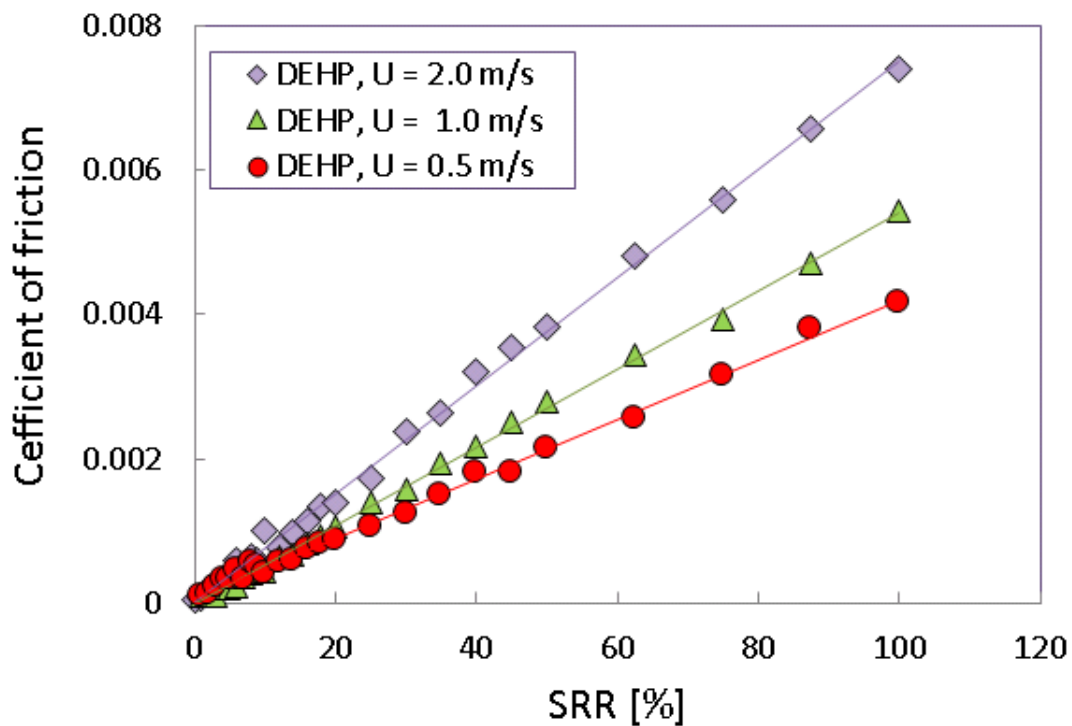


Fig. 6.2: MTM soft contact traction curve, 10N, PMMA disc, DEHP at 40°C

In order to extract more information from the data, traction curves are converted to stress-strain curves using Eq. 6.1 and 6.2.

$$\dot{\gamma} = \frac{SRR \times U_e}{h_c} \quad (6.1)$$

$$\tau = COF \times \bar{P} \quad (6.2)$$

The mean pressure, $\bar{P}$, can be calculated from the Hertz equations using the reduced elastic modulus measurements described in Chapter 5.

In principle, the film thickness values are available directly from optical interference measurements as described in the previous chapter and this was the case for the hydrocarbon-based lubricants studied. Unfortunately it was found that the phthalate ester DEHP partially dissolved the polymer disc surface, leading to very rapid loss of the semi-reflective chromium coating so it was not possible to obtain interferometric film thickness images for this fluid.

Figure 6.3 shows friction results for GTL8 using the same test conditions as in figure 6.2 while figure 6.4 shows mean shear stress versus strain rate curves calculated from these results. All of the results at different entrainment speeds collapse on to a single shear stress-strain rate curve. Given the extremely low friction coefficients obtained in each test, this is quite remarkable and lends credence to the method.

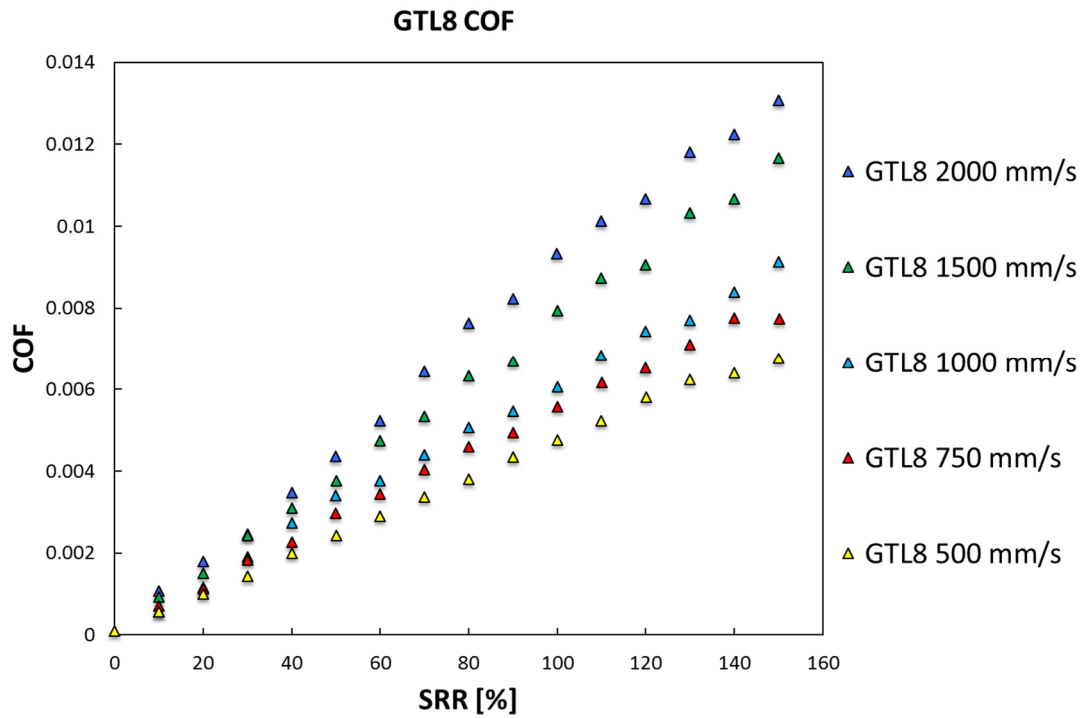


Fig. 6.3: Coefficient of friction of GTL8 for different entrainment speeds

Figure 6.4 compares shear stress *versus* strain rate results for the three hydrocarbon fluids, GTL4, GTL8 and squalane.

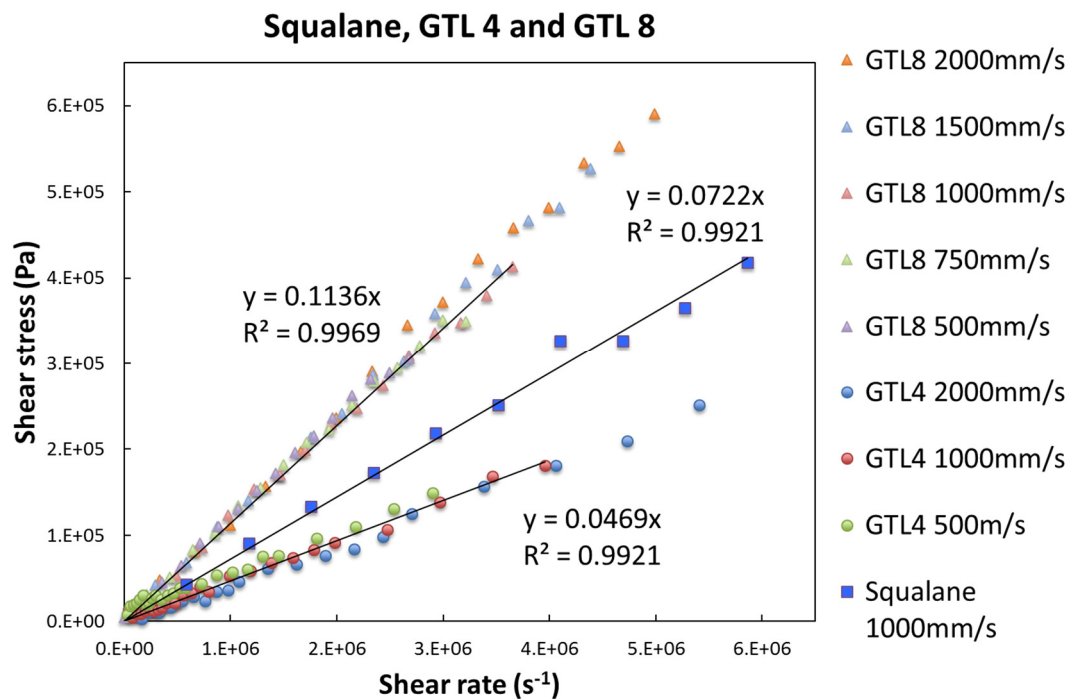


Fig. 6.4: Stress-strain curves, 10N, PMMA disc, GTL4 and GTL8 at 40°C

There is a clear difference between the shear stress values of the three oils, as expected from their different viscosities. The SVM viscosities of the three base oils are 14.8, 15.2 and 35.8 cP for GTL4, squalane and GTL8 respectively at 40C. The difference between squalane and GTL4 is greater than implied by their viscosities but it should be noted that squalane has a higher pressure viscosity coefficient which will lead to an increase of in-contact viscosity.

From the measured shears stress - strain rate behaviour and Eq. 6.3 it is possible to deduce an in-contact viscosity at a temperature of 40°C.

$$\tau = \eta_{in-contact} \times \dot{\gamma} \quad (6.3)$$

The actual in-contact viscosity can be calculated from Eq. 6.4 where η_{atm} is the measured value from the SVM and the mean contact pressure is determined by the Hertz equations and is 45.2 MPa for a 10 N load on PMMA.

$$\eta_{in-contact} = \eta_{atm} \times e^{\alpha \bar{P}} \quad (6.4)$$

Results from the SVM and those calculated from shear stress measurements in the MTM are compared in table 6.1.

Table 6.1: Squalane, GTL4 and GTL8 viscometric in-contact data

	<i>SVM: η_{atm}(cP)</i>	<i>SVM: $\eta_{in-contact}$(cP)</i>	<i>MTM: $\eta_{in-contact}$(cP)</i>	<i>Ratio MTM/SVM</i>
GTL 8	35.8	70.5	113.6	1.61
GTL 4	14.8	27.9	46.9	1.88
Squalane	15.13	34.3	72.2	2.10

There is a large discrepancy between the values calculated from viscosity measurements and those from MTM friction measurements with the values from

friction measurements being 60 to 100% greater than those calculated from the viscosity. The discrepancy is larger for GTL4 than for the higher viscosity GTL8.

6.2 POSSIBLE SOURCES OF ERROR

Several possible sources for this discrepancy have been explored.

1. Effect of not applying a semi reflective chromium layer on the MTM discs

A chromium layer could theoretically affect results by increasing the Young's modulus of the polymer disc or by improving heat transfer.

The layer's thickness is however so thin (20nm) that any effect on the Young's modulus is negligible. In fact, by applying the numerical results of Cole *et al*'s model [1] for the effect on pressure and contact size of an indented two layer surface material it can be found that the chromium coated disc is expected to behave like a pure polymer disc.

The friction is very low such that an increase in temperature due to friction is negligible. If any heating effects were to occur in the current experimental setup without a chromium layer, it would be impossible to overlap stress strain curves of tests implementing different entrainment speeds as shown in figure 6.4 and the discrepancy between theoretical results and experimental results would be increased. Nevertheless, by applying Kadiric *et al*'s model [2] to the contact it can be found that even if a temperature effect were to occur, the heat transfer of the chromium coated disc is that of a pure polymer disc.

2. MTM calibration for low loads and ultra low friction

The MTM is designed to measure elastohydrodynamic friction coefficients which are generally an order of magnitude greater than those present in hydrodynamic conditions. To measure hydrodynamic friction at the loads employed, a resolution of 0.01N is required which requires careful calibration.

In a static calibration setup, several weights of 1g to 50g were suspended via a calibration pulley in order to verify sensitivity and magnitude of friction calculated from the MTM strain gauge measurement system. The entire strain gauge system is

connected to the loading arm that also serves the purpose to rotate the ball. All measurements appeared accurate. Also the load calibration was verified in this manner. Furthermore, the friction sensor was tested in a dynamic test, by adding supplementary weights pulling horizontally on the rotating arm in line with the friction sensor. The friction difference measured during the test between adding and removing a horizontal force corresponded to the actual additional force applied. It should be noted that in order to run this experiment successfully, the positioning along the shaft of the additional horizontal load needs to be calibrated in order to account for the moment applied to the friction sensor.

3. Test rig error

Tests were conducted on two different MTM2s. The results are compared in figure 6.5. It can be seen that there is a good match between results from two different test rigs

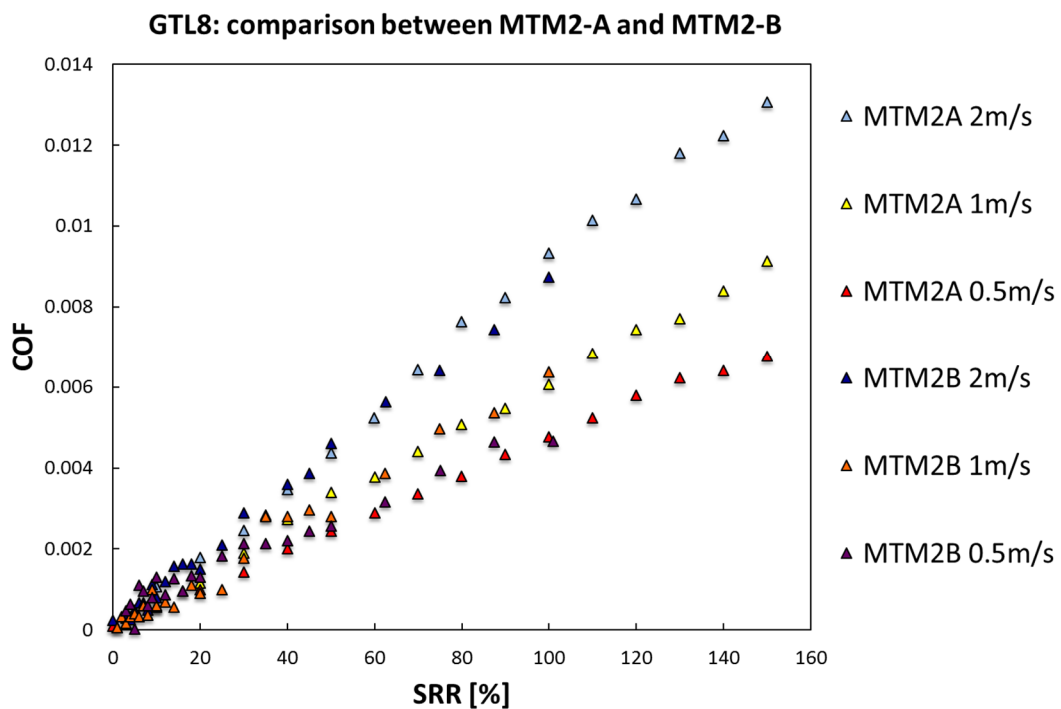


Fig. 6.5: MTM2 comparison, GTL8 10N, 40°C

MTM2-B proved to be less accurate due to poorer maintenance of the machine. Nevertheless, the coefficient of friction matches quite closely between the two different

test rigs. Thus the discrepancy between viscometer-derived and friction derived-viscosity values does not arise from a specific, unidentified test rig problem.

4. Polymer disc-related error

Traction force measurements using squalane in a steel ball-polycarbonate disc contact are presented in figure 6.6. Various loads were used. Mean shear stress versus strain rate results are deduced in figure 6.7 by calculating strain rates from experimentally-acquired film thickness data. The differences between the MTM-friction method and the SVM viscometer method are presented in table 6.3.

The Young's modulus of polycarbonate was obtained by the same method as described in Chapter 5 and the properties are listed in table 6.2.

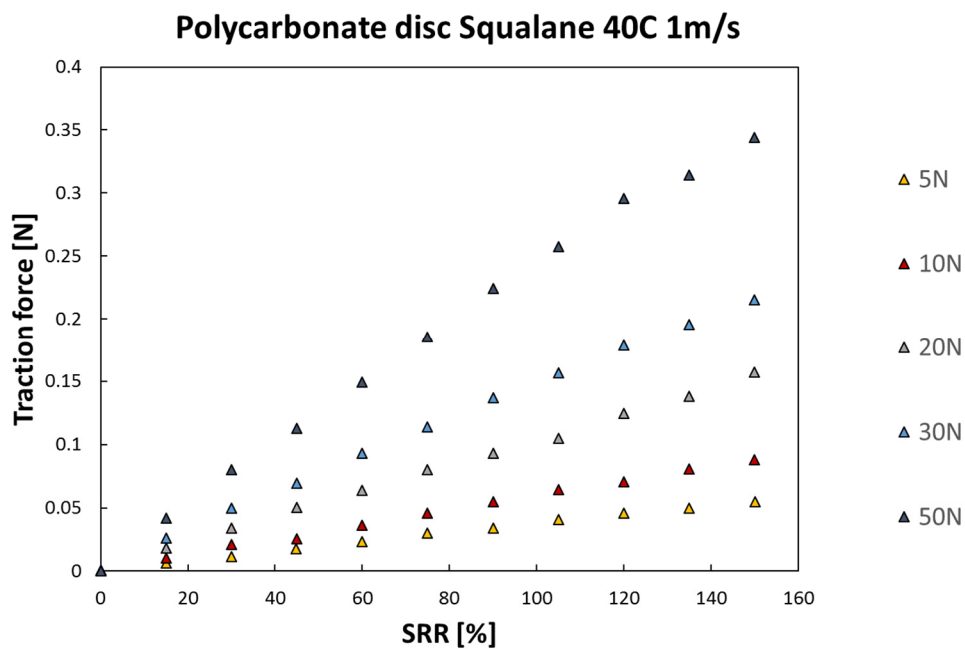


Fig. 6.6: Measured traction force against slide-to-roll ratio for different loads

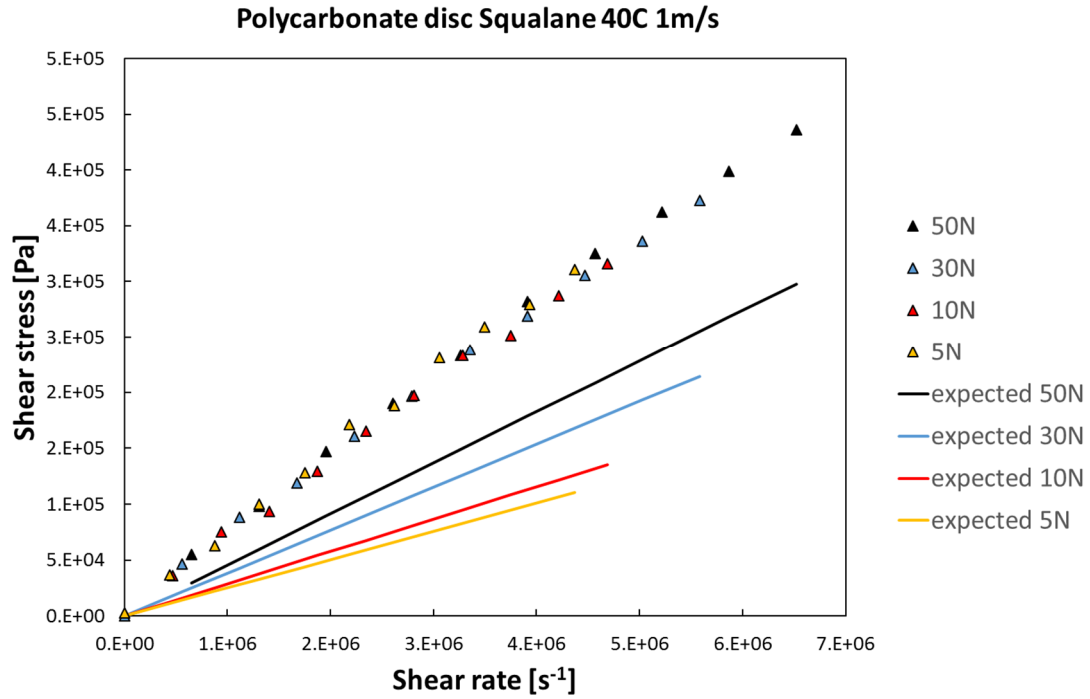


Fig. 6.7: Expected and measured stress against strain for different loads

Table 6.2: Properties of polycarbonate

	E (GPa)	ν
Polycarbonate	2.4	0.37

Table 6.3: Squalane, viscometric in-contact data for different loads

	η_{atm} (cP)	$SVM \eta_{in-contact}$ (cP)	$MTM \eta_{in-contact}$ (cP)	Error factor
Squalane 5N	15.1	25.3	73.6	2.91
Squalane 10N	15.1	28.9	70.0	2.42
Squalane 30N	15.1	38.4	70.4	1.83
Squalane 50N	15.1	45.7	70.3	1.54

It appears that also for a polycarbonate disc, large differences between theory (obtained by SVM) and experimental measurements (obtained by MTM) occur. The error factor decreases with increasing load.

3. Viscous drag (friction in the meniscus outside of the Hertzian region)

Measured friction is extremely small, typically below 0.1N or even below 0.01N depending on the load and sliding speed applied. Hence, hydrodynamic friction may not necessarily be dominated by the in-contact friction but could also include out viscous drag.

Viscous drag may be calculated by the following equations:

$$F = \int_a^{na} 2\pi r \tau dr \times \frac{2}{3} \quad (6.5)$$

$$\tau = \eta_0 \frac{v}{h} \quad (6.6)$$

na is chosen by the user according to the thickness of the oil drag around the contact. The factor $2/3$ comes from the wake of the contact as can be seen in the fluorescence images in Chapter 5.2. The wake being without oil, it does not contribute to the out-of-contact viscous drag. Viscous drag is proportional to sliding speed, thus also to shear rate or slide to roll ratio.

Figure 6.8 shows the expected stress resulting from drag and compares it to the expected stress from the in-contact friction. It was estimated that the oil film outside of the contact would reach 1.3mm. As load is increased, the viscous drag increases, however the film thickness reduces more. Hence, overall the stress to strain rate relation of viscous drag reduces with increasing load.

Revising the expected stress strain equation and applying it to the experiments in figure 6.7, it is possible to deduce figure 6.9.

Stress strain curves appear closer to the experimental value, however another overall factor of about 1.5 still remains.

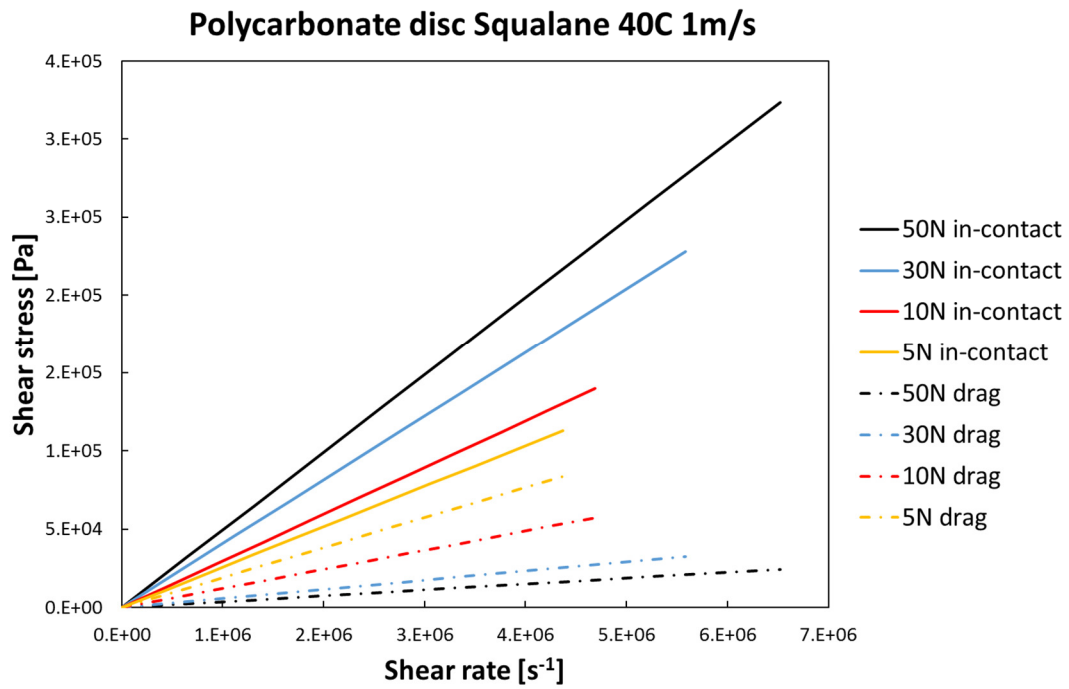


Fig. 6.8: Expected viscous drag and in-contact stress against strain for different loads

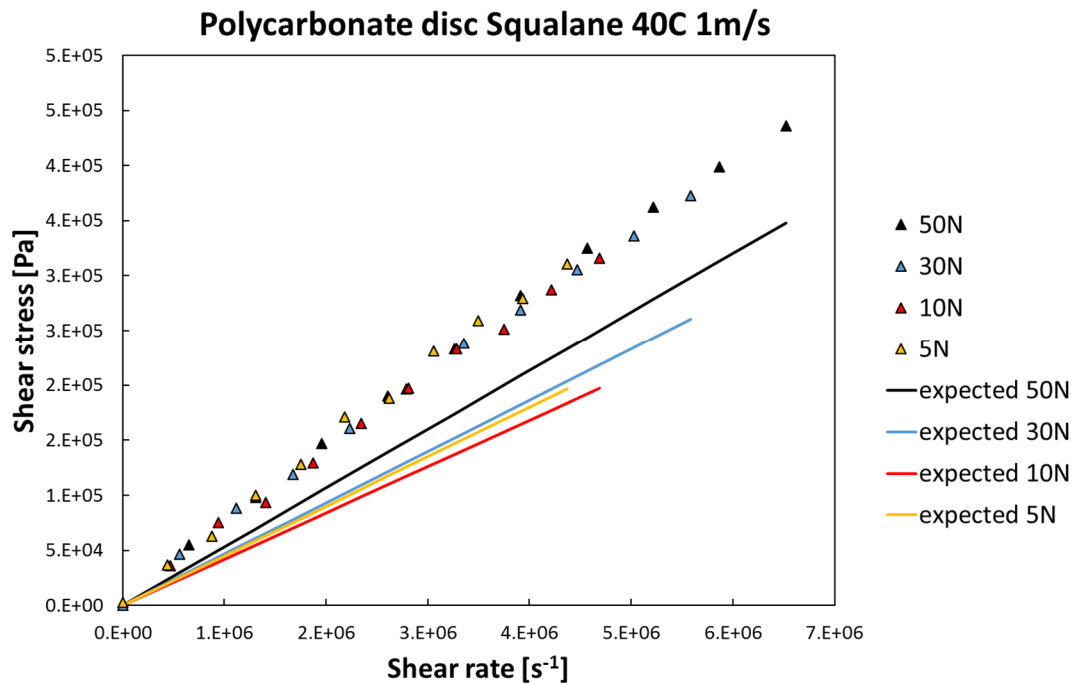


Fig. 6.9: Revised expected total stress including viscous drag and measured stress against strain rate for different loads

5. Solid to solid contact

One possibility for the higher than predicted friction is that there is a significant solid-solid contact and thus boundary friction component. This is very unlikely since optical interferometry shows the formation of thick, fully-separating films in an identical contact geometry and conditions. It was, however, noted that in the MTM two wear tracks appeared on the polymer disc. These occurred at the sides of the contact (see figure 6.10) and grew over running time.

Several wear tests have been conducted and led to the conclusion that tracks could only influence the friction measurement once they exceed 50 nm in depth and in that case the error would be of the order of 10%. In the work carried out in the current study all wear tracks were well below 50 nm.

It is probable that the tracks were formed from microcracks resulting from cyclic deformation of the disc in the ball on disc contact at the large stress gradients at the edges of the contact.

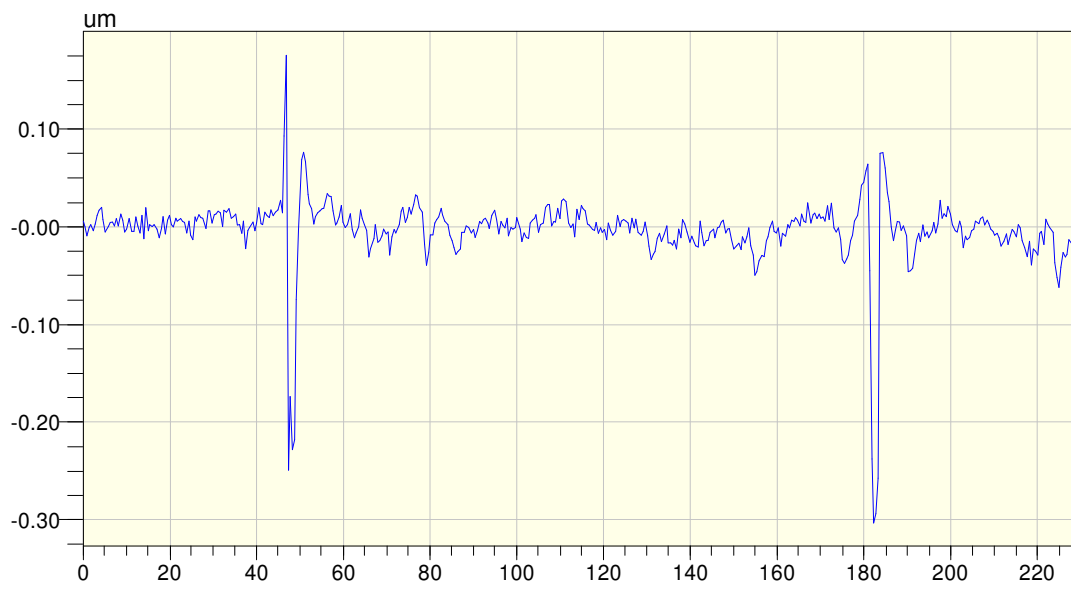
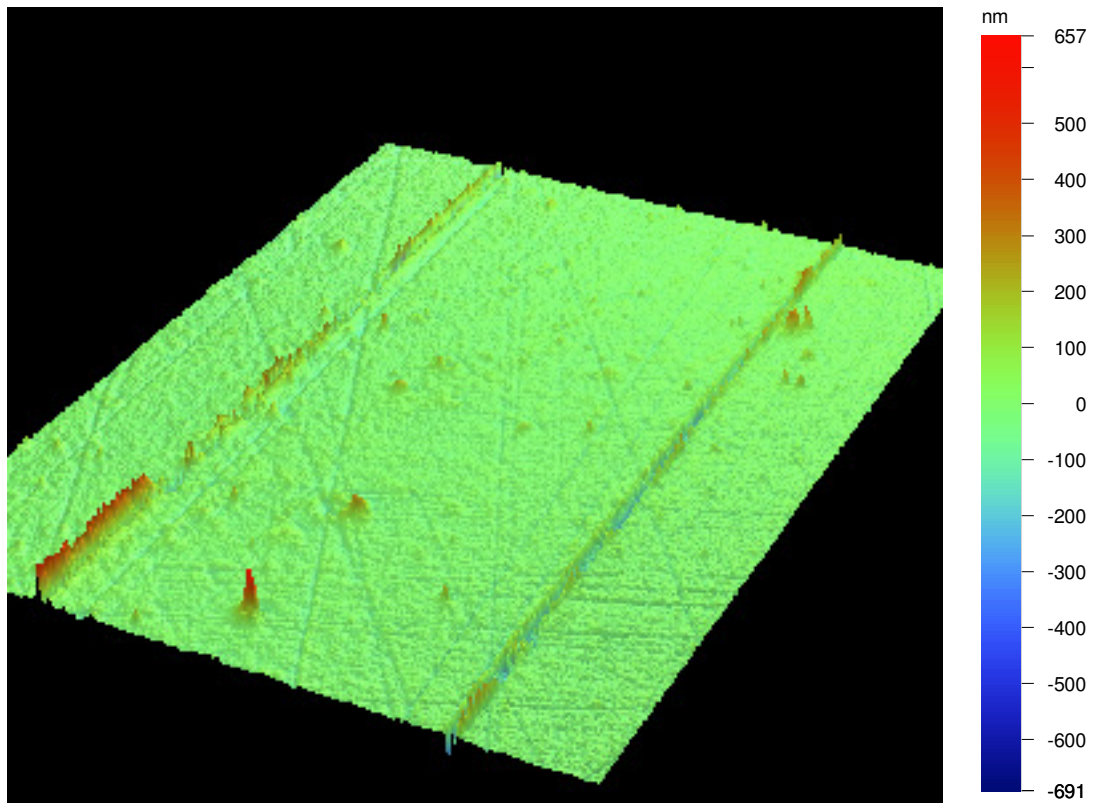


Fig. 6.10: Deeper wear tracks for which a 10% error in friction was measured.

6. Viscoelastic effects

One possibility is that the higher than predicted shear stress from friction measurements originated from viscoelastic behavior of the polymer disc.

There are several ways these might manifest. One is via a change in contact area due to viscoelastic disc response that leads to changes in contact pressure. Figure 6.11 shows interference images of pure rolling contacts for squalane, GTL4 and GTL8 at 1 m/s and a load of 10 N, as well as a statically loaded 10 N contact. The results were obtained from two EHD test rigs rig using different cameras. Nevertheless, the static contact size and shape are the same.

Three phenomena can be observed:

- (a) The shape of the dynamic contact is not circular. It resembles an oval mirrored D-shape.
- (b) The contact size is smaller for running conditions than for static conditions at a same load, suggesting a stiffer contact
- (c) The size reduction depends on the oil used, its viscosity and its pressure viscosity coefficient.

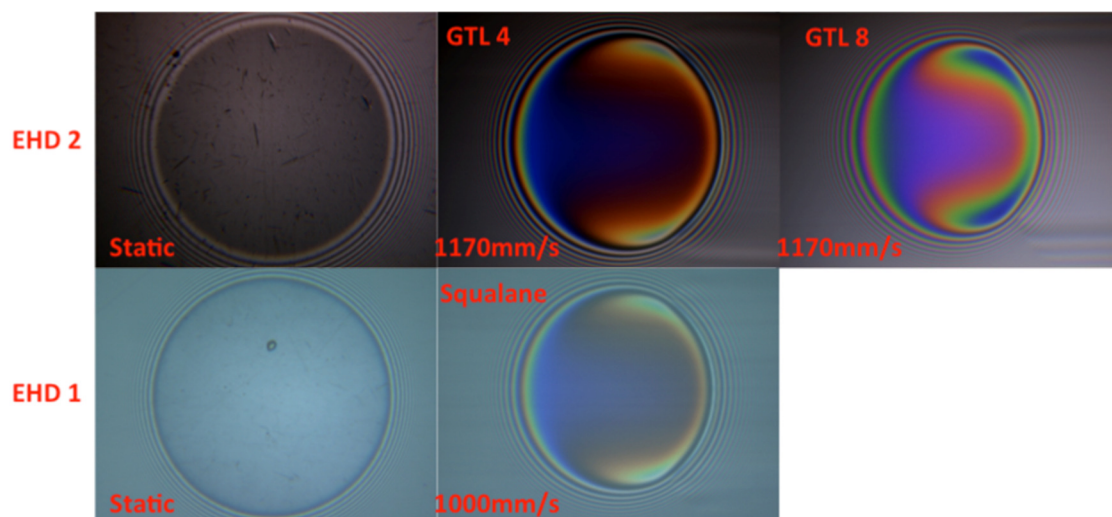


Fig. 6.11: Static, 1m/s PMMA disc, pure rolling 10N: Squalane, GTL4, GTL8

Figure 6.12 compares images in tests of squalane in a steel ball on polycarbonate disc setup and a steel ball on PMMA disc setup at identical load and speed conditions. The

contact size reduction is significantly larger for the PMMA disc than the polycarbonate one.

It is interesting to see that the size reduction for a polycarbonate disc is less apparent than that of PMMA, even though the polycarbonate disc forms a thicker film due to its slightly lower Young's modulus.

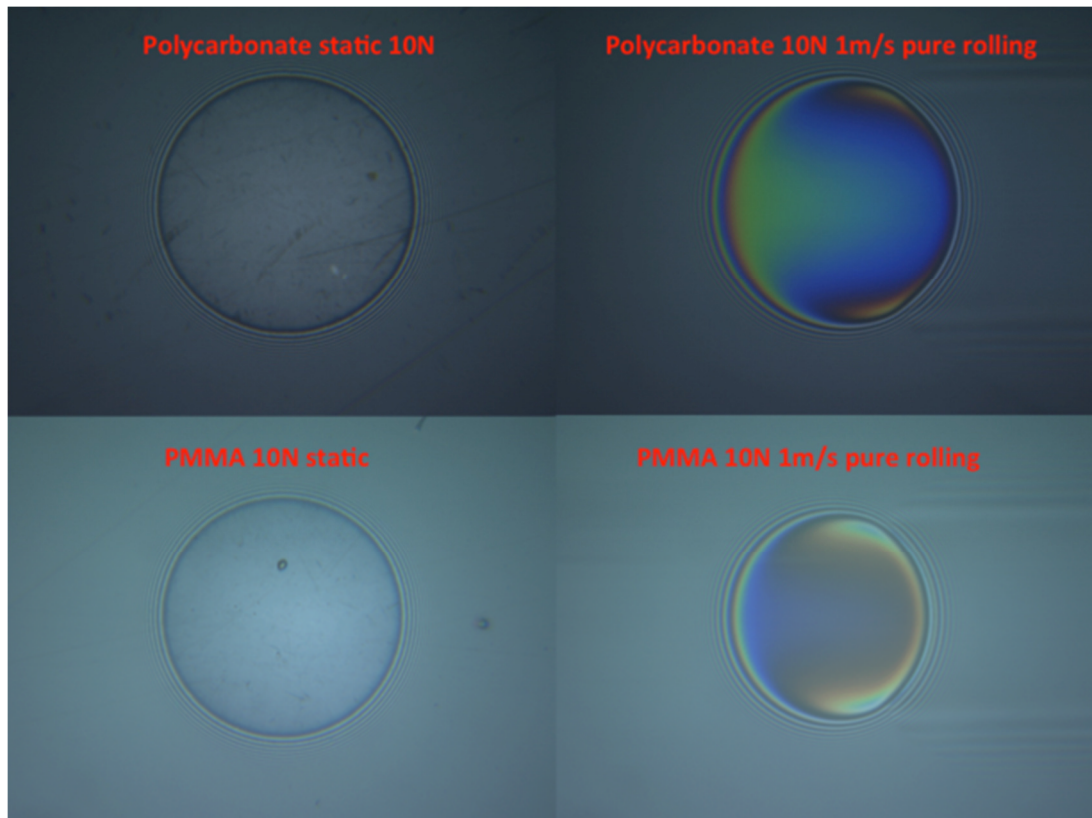


Fig. 6.12: PMMA vs polycarbonate disc, static and 1m/s pure rolling 10N, Squalane

The oval D-shape of PMMA can be explained by viscoelastic effects in which the PMMA stiffens in the direction of shear. The stiffening effect is different between the two materials, most likely due to the difference in their viscoelastic properties.

It is interesting to note that the contact size reduction (and thus the presumed stiffening effect) for PMMA depends on SRR (see Figure 6.13) and on entrainment speed (see figure 6.14). Hence, the rate of loading has an effect on the contact, as one would expect for viscoelastic materials.

In particular in the case of positive SRR, the contact size reduces compared to negative SRR. For positive SRR the disc travels faster than the ball. Consequently the viscoelastic material travels faster and stiffens more.

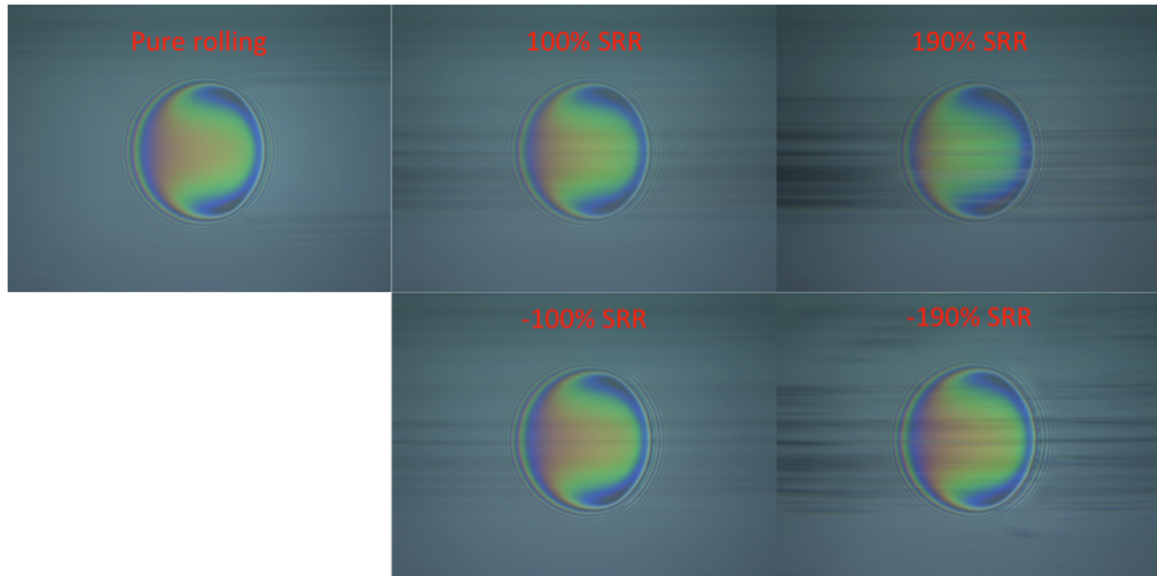


Fig. 6.13: PMMA, Squalane, 10N, SRR>0: disc faster than ball, SRR<0: ball faster than disc

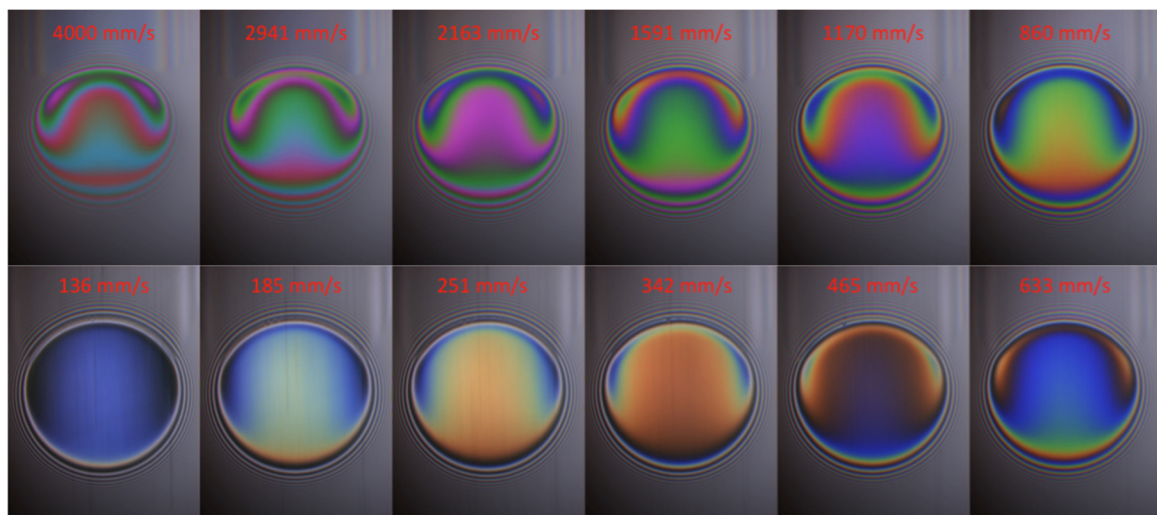


Fig. 6.14: PMMA, GTL 8, 10N, pure rolling

Table 6.4 compares the properties at 40C of Squalane, GTL4 and GTL8.

Table 6.4: Viscometric properties at 40C of Newtonian lubricants

	Squalane	GTL 4	GTL 8
$\eta_{atm}(cP)$	15.2	14.8	35.8
$\alpha (GPa^{-1})$	18	14	15

Table 6.5 compares the contact size and its reduction from the static contact for each case.

Table 6.5: Contact area at 1m/s 10N PMMA disc

10N, 1m/s PMMA	Static	Squalane	GTL 4	GTL 8
Contact area A (mm^2)	0.221	0.152	0.174	0.135
Compared to Hertz (%)	99.9	68.8	78.5	60.9
Mean contact pressure (MPa) $\bar{P} = F/A$	45.2	65.6	57.5	74.2

The contact size reduction leads to higher than Hertzian contact pressures. The actual mean contact pressure may be found from the load applied and the contact area.

Figure 6.15 revises figure 6.4 by adjusting the contact pressure. However even by adjusting contact pressures, no sensible comparison between MTM and theoretical results of the in-contact viscosity could be found as can be seen by the new error factors in table 6.6.

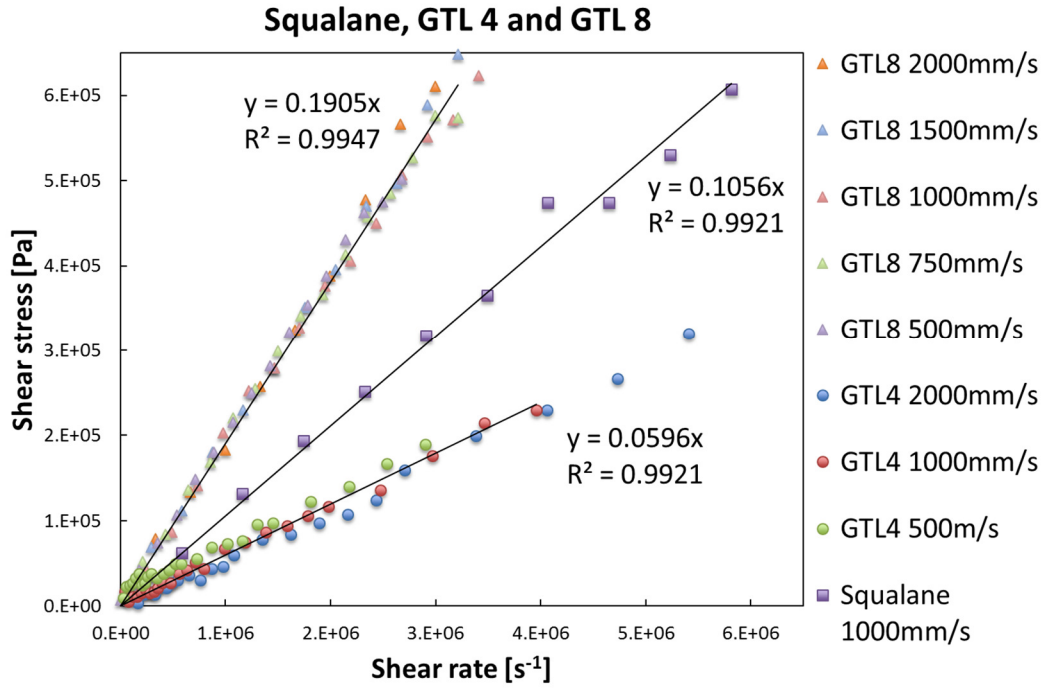


Fig. 6.15: Revised pressure applied to figure 6.4

Table 6.6: Error factors for revised pressure

	$\eta_{atm}(cP)$	$SVM \eta_{in-contact}(cP)$	$MTM \eta_{in-contact}(cP)$	Error factor
GTL 8	35.8	109.0	190.5	1.75
GTL 4	14.8	33.1	59.6	1.8
Squalane	15.2	49.5	105.6	2.13

In order to verify how viscoelasticity affects friction the MTM was run in the bidirectional mode. Thereby traction is measured in four different scenarios.

1. $T_1 : U_{ball} > U_{disc} > 0$
2. $T_2 : U_{disc} > U_{ball} > 0$
3. $T_3 : U_{disc} < U_{ball} < 0$
4. $T_4 : U_{ball} < U_{disc} < 0$

It is thus possible to obtain Couette friction in 4 ways:

1. $\frac{T_1 - T_2}{2}$
2. $\frac{T_4 - T_3}{2}$
3. $\frac{T_1 - T_3 - 2F_r}{2}$
4. $\frac{T_4 - T_2 + 2F_r}{2}$

When the direction of speed is changed, this induces twice the rolling friction F_r on the strain gauges, where $2F_r = T_2 - T_3 = T_4 - T_1$.

In calculation method 3 the polymer disc spins faster than in calculation method 4. Thus the speed at which viscoelastic material enters the contact differs.

Figure 6.16 shows the experimental results for all four methods to obtain the coefficient of friction against SRR while using the revised pressure. All methods overlap and thus suggest only small effects of SRR dependent viscoelastic effects on friction as suggested in the film thickness measurements in figure 6.13. Due to this overlap also hysteresis effects on friction may be ruled out. It is possible that entrainment deformation plays a larger role.

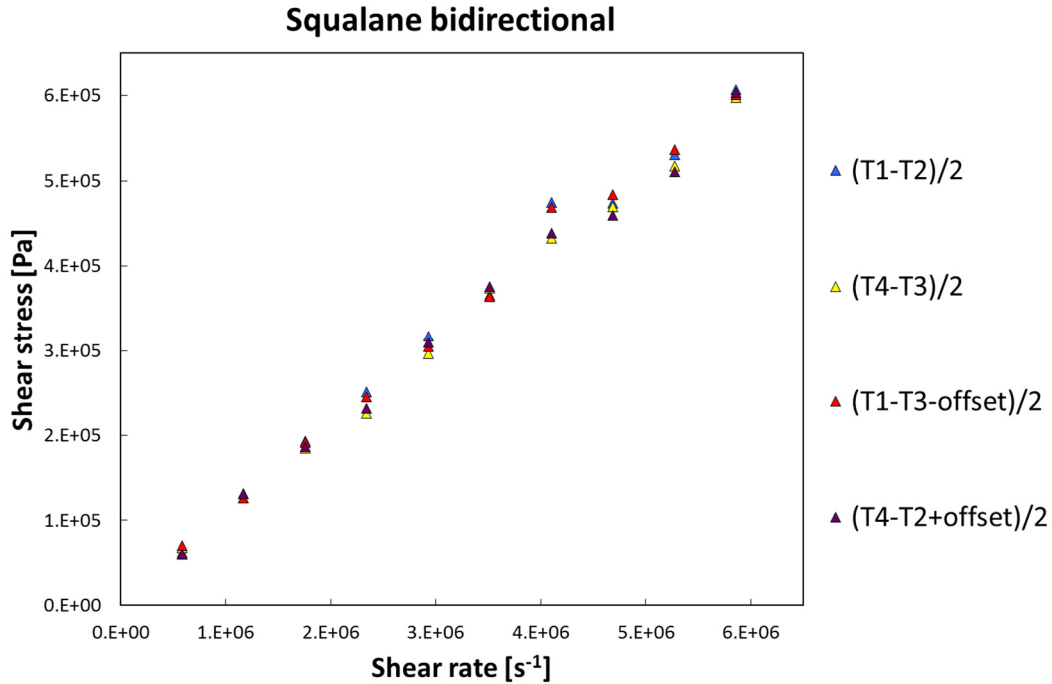


Fig. 6.16: Bidirectional results, Squalane, 10N, PMMA

Unfortunately no match between existing theory and experiment could be obtained.

Three causes have been identified:

1. incorrect calculation of contact pressure, which has been accounted for
2. deformation of the contact: viscoelastic effects on the polymer disc due to the entrained oil and contact conditions, which have not been accounted for.

7. Alternative method to measure friction and film thickness

Discrepancy could also occur from the fact that the EHD rig and the MTM rig apply slightly different conditions to the experiment for a soft contact.

In order to verify this a new setup was assembled: the self designed custom manufactured ultra-low runout platform and inverted interferometric microscope were fit to the CETR tribometer as shown by figure 6.17. This would allow to measure friction and film thickness simultaneously for the same contact. Unfortunately, however, friction was found to be off by one order of magnitude. It was found that although the CETR has a measurement platform that is able to measure to extremely high accuracies (as low as 0.02N), its designed spring damper system that holds the specimen affects the friction measurement.

As load is applied, a small proportion of the load affects the measurement of the frictional measurement component for a statically loaded contact. Different specimen holder geometries and different springs were tested with the same result.

For a dynamically loaded contact, hydrodynamic friction in the contact misaligns the spring. Thus a different factor of the load is found in the friction measurement. This factor is highly dependent on load, film thickness and entrainment speed, thus the rig is deemed not appropriate to measure hydrodynamic friction.

Finally the MTM remains to be the most reliable rig to measure hydrodynamic friction.

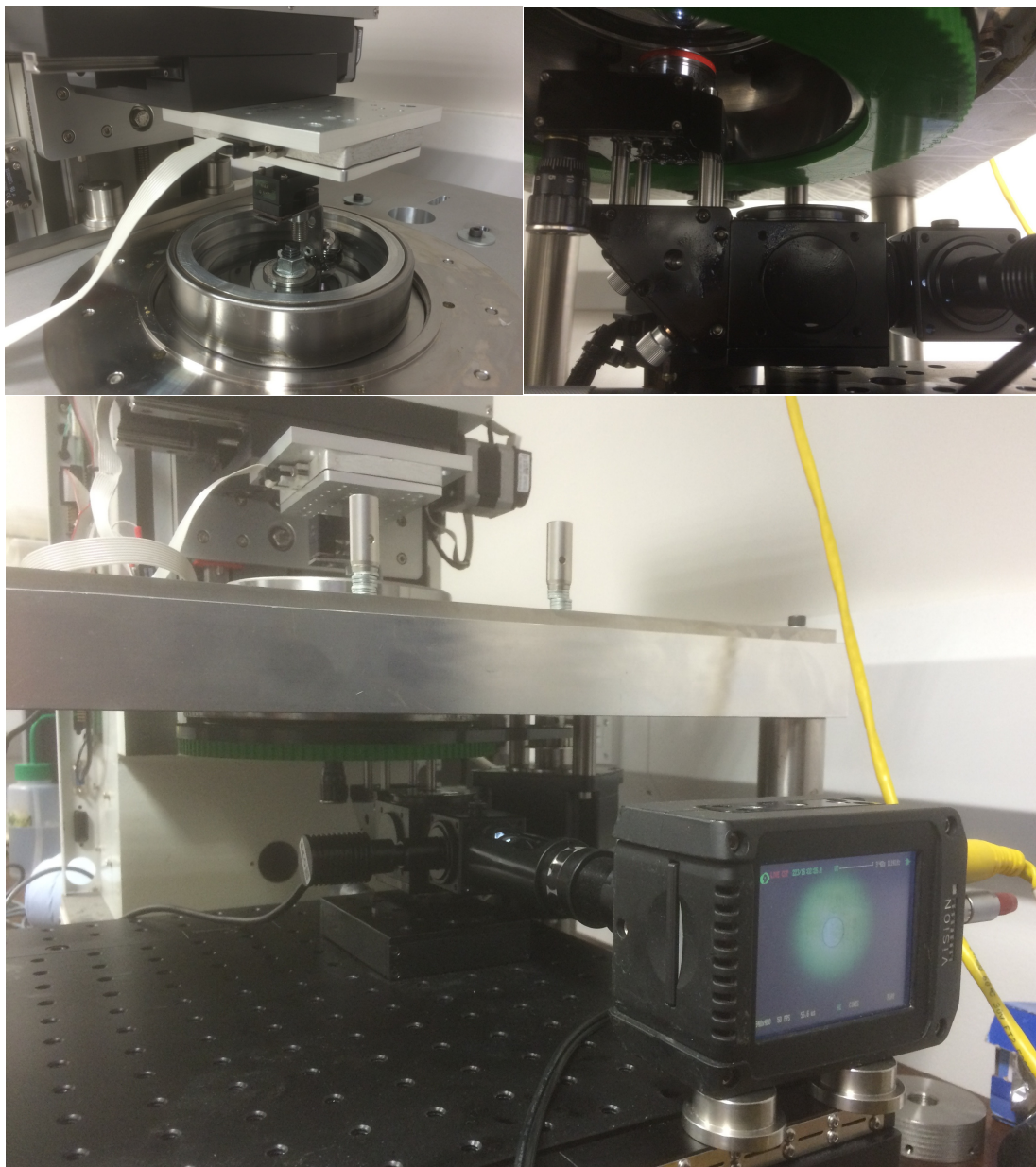


Fig. 6.17: CETR tribometer, interferometric optical setup and the ultra-low runout platform.

6.3 TO SUMMARISE THE FINDINGS

- It is possible to measure hydrodynamic friction with a soft contact applied to the MTM.
- The MTM measures higher friction and thus higher stress against strain rate than expected.
- The MTM is calibrated and able to produce accurate friction data even for ultra low friction.
- Friction data obtained from two different MTMs give the same results.
- Contact size and deformation is load dependent, viscosity dependent, pressure viscosity coefficient dependent and dependent on the viscoelastic properties of the polymer disc.
- It is suspected that this deformation contributes to friction and is dependent on the same parameters but to a different extent.
- Viscous drag affects the friction and thus the stress value obtained. This can be accounted for, however it is not the sole factor between theory and experiment.

In order to use the MTM as a stress strain measurement device, in the following solely PMMA discs will be used at a load of 10N. When comparing theory to experiment for friction measurements, oils featuring similar orders of magnitude in viscosity and similar pressure viscosity coefficients will be used. This will be achieved by blending GTL4 oils to an equivalent low shear viscosity as that of GTL8. Viscous drag and other offset factors will thus be equivalent to each other.

Finally a factor of 1/1.8 will be attributed to the stress measured on these GTL blends.

For hydrodynamic film thickness measurements in these soft contacts piezoviscous effects, viscoelastic effects and viscous drag do not affect the measurements and no scaling factors are necessary. Thus, a large variation of oils may be studied for hydrodynamic film thickness in full depth.

References

- [1] Cole, J.S., Sayles, R.S.: A numerical model for the contact of layered elastic bodies with real rough surfaces. ASME. J. Tribol. 114(2), pp.334-340, (1992)
- [2] Kadiric, A., Sayles, R.S., Ioannides, E.: Thermo-mechanical model for moving layered rough surface contacts. ASME. J. Tribol. 130(1), pp. 011016-1-14 (2008)

7 Shear thinning in model lubricated contacts

This chapter assembles all of the techniques developed and applies them to the study of shear thinning, polymer-containing oils. An overlap of experimental conditions between the techniques is ensured in order to be able to combine the results in Chapter 8. Accurate flow curves are obtained for the studied oils. In the model hydrodynamic contact a reduction in film thickness and friction is observed for shear thinning oils when compared to Newtonian oils. Thus shear thinning oils adapt to contact conditions.

Now that the new techniques to investigate hydrodynamic film thickness and friction have been established, as described in Chapters 5 and 6, it is possible to investigate shear thinning of VM solutions. The three processes to investigate shear thinning are:

1. flow curve measurement
2. hydrodynamic film thickness measurement
3. hydrodynamic friction measurement

A testing temperature of 40°C was found to provide a good overlap between all experimental setups. Thus all experimental measurements in this Chapter are obtained at 40°C.

7.1 OBTAINING FLOW CURVES

Flow curves are obtained as described in Chapter 4.

The viscosity modifiers studied can be divided in to three different groups: model polymers, engine oil viscosity modifiers and gear oil viscosity modifiers.

For several shear thinning oils, Newtonian oils are shown in the flow curves corresponding to the two Newtonian plateaus of the shear thinning oil. These are later implemented in order to show the reduction in film thickness and friction that is obtained due to shear thinning from the first Newtonian plateau and to show how much the viscosity modifier is still able to thicken the oil compared to the second Newtonian plateau, its base oil. For figures 7.2 and 7.3, both Newtonian plateau equivalent lubricants are shown, for figures 7.1, and 7.4-8 only the base oil viscosity is included.

7.1.1 FLOW CURVES OF MODEL POLYMERS

Two types of model viscosity modifiers were used: polystyrene and polyisoprene.

Figure 7.1 shows the flow curves of 10%wt 50k g/Mol PS in DEHP, 4%wt 100k g/Mol PS in DEHP and 2%wt 200k g/Mol PS in DEHP.

Figures 7.2 and 7.3 show the same flow curves for the same 200k and 50k g/Mol solutions referenced against the base oil and respective equivalent low shear viscosity oils featuring Newtonian behaviour. One is a mixture of PAO45-400, the other is a PAO10.

Figure 7.4 shows the flow curve of 3%wt 100k g/Mol polyisoprene in squalane which, however, is degraded to 30k g/Mol as shown in the GPC results in Chapter 4.

Table 7.1 lists the Carreau Yasuda (CY) parameters obtained by fitting the CY model to the experimental data of the model polymers.

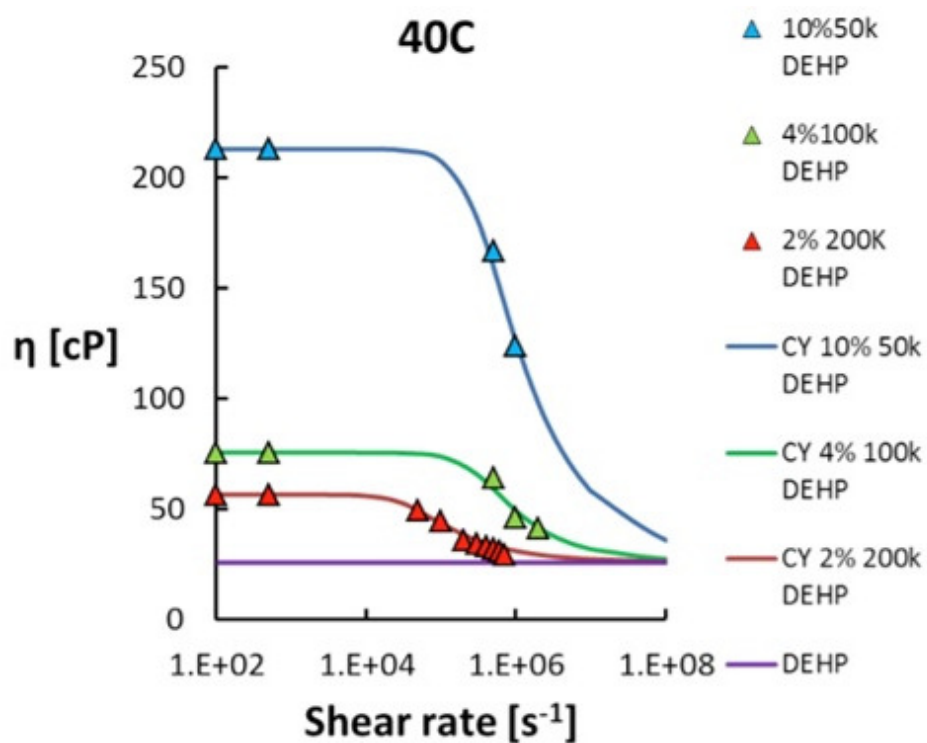


Fig. 7.1: Polystyrene solution viscosity modifiers, Carreau Yasuda fit

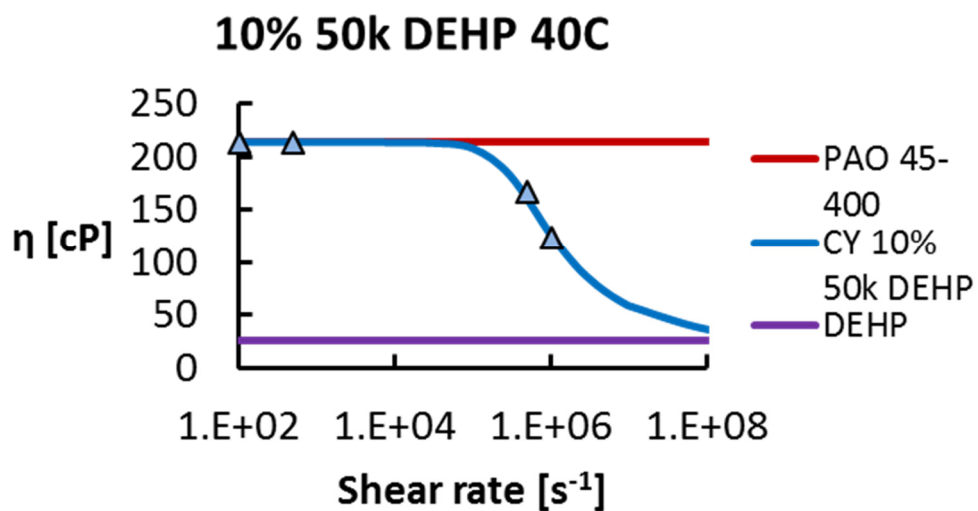


Fig. 7.2: PAO45-400, DEHP and 10% 50k g/Mol PS in DEHP, Carreau Yasuda fit

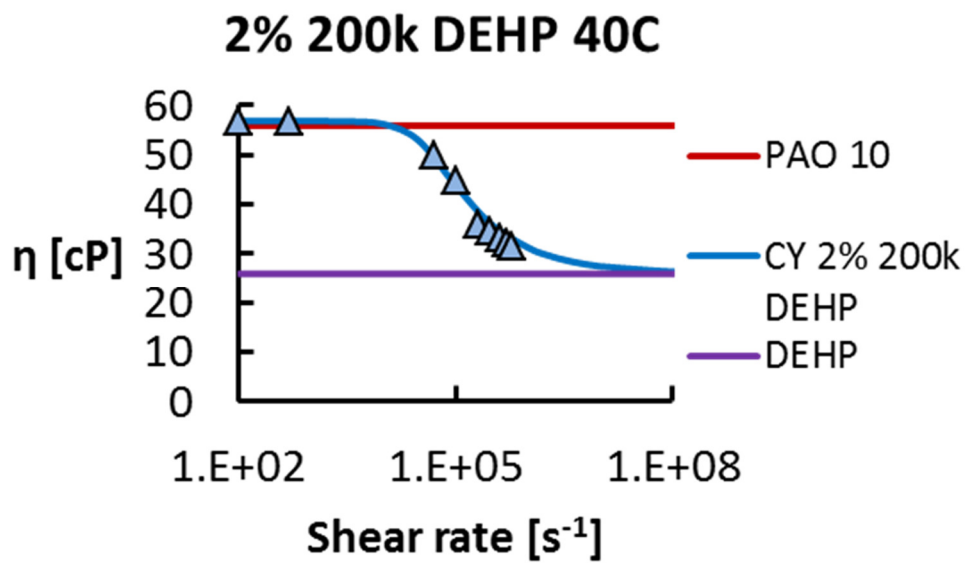


Fig. 7.3: PAO10, DEHP and 2% 200k g/Mol PS in DEHP, Carreau Yasuda fit

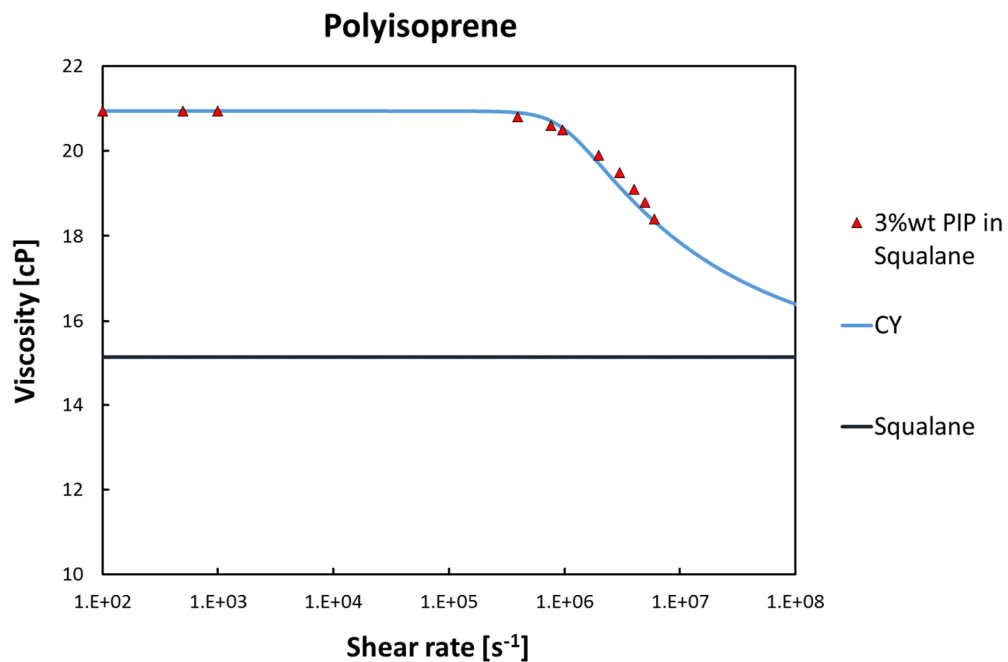


Fig. 7.4: 3%wt PIP in squalane and squalene, Carreau Yasuda fit

Table 7.1: CY parameters for model polymer solutions

	η_0 (cP)	η base (cP)	A (s)	n	a
10% 50k PS	213.40	26.06	6.67E-06	0.6	3
4% 100k PS	75.67	26.06	1.25E-05	0.6	3
2% 200k PS	56.88	26.06	5.00E-05	0.4	3
3% 100k PIP (30k)	20.95	15.13	1.00E-06	0.67	3

7.1.2 FLOW CURVES OF ENGINE OIL VISCOSITY MODIFIERS

Figure 7.5 shows the behaviour of three different viscosity modifier blends, containing OCP, HSD di-block and HSD star polymers, diluted in GTL4 at concentrations to achieve an equivalent low shear viscosity the same as GTL8. Their shear thinning behaviours are similar.

Figure 7.6 shows the flow curve for a very high concentrated OCP diluted in GTL4. The higher concentrated blend shear thins at noticeably lower shear rates than the lower concentrated blend. This is expected due to the elevated shear stress the high concentration blend experiences.

Table 7.2 lists the Carreau-Yasuda parameters derived from fits to the respective experimental data of the engine oil viscosity modifiers. The second Newtonian viscosity in this and subsequent fits is assumed to be that of the base oil.

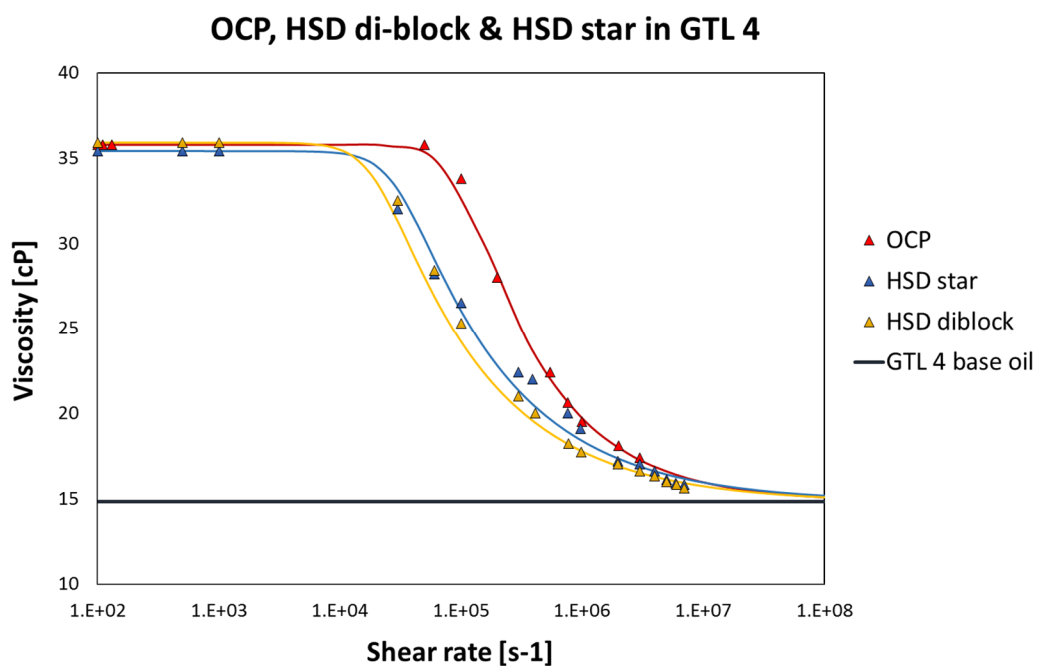


Fig. 7.5: 0.88%wt OCP, 1.53%wt HSD di-block and 1.64%wt HSD star VMs in GTL4 and GTL4, Carreau Yasuda fit

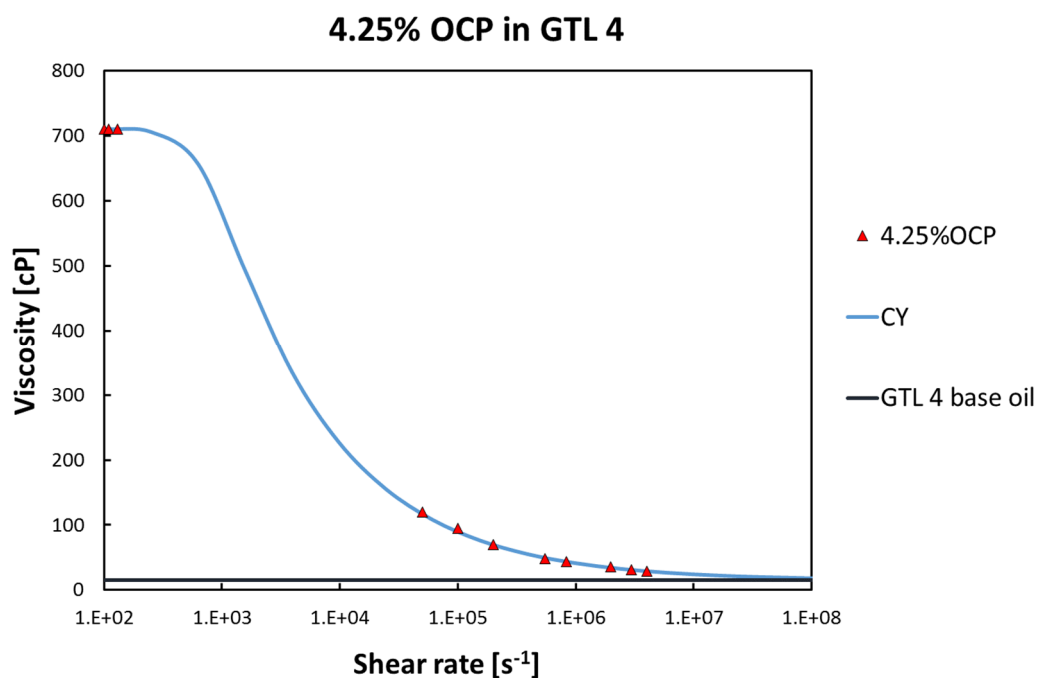


Fig. 7.6: 4.25%wt OCP in GTL4, Carreau Yasuda fit

Table 7.2: CY parameters, engine oil VMs

	η_0 (cP)	η base (cP)	A (s)	n	a
0.88% OCP	35.8	14.8	2.5E-04	0.37	3
1.52% HSD di-block	35.9	14.8	5.0E-05	0.5	3
1.64% HSD star	35.4	14.8	3.3E-05	0.5	3
4.25% OCP	710	14.8	1.4E-03	0.55	3

7.1.3 FLOW CURVES OF GEAR OIL VISCOSITY MODIFIERS

Only one gear oil viscosity modifier was tested, PMA. Again concentration was adjusted to feature a similar low shear viscosity as GTL8. However, in order to see more shear thinning in the flow curve, PMA was diluted in GTL3 instead of GTL4. GTL3 has about half the viscosity of GTL4, thus in order to thicken the oil up to a GTL8 oil the polymer content is significantly increased.

Figure 7.7 shows the flow curve for the described PMA/ GTL3 blend and figure 7.8 shows the flow curve of a different PMA/ GTL3 blend which contains double the PMA concentration.

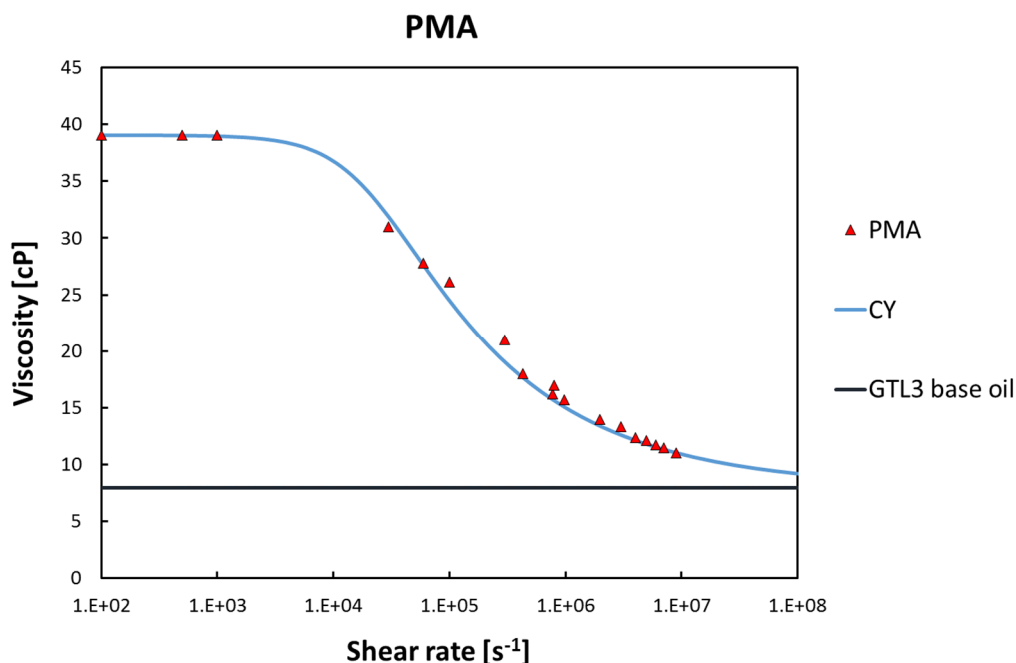


Fig. 7.7: 14%wt PMA in GTL3, Carreau Yasuda fit

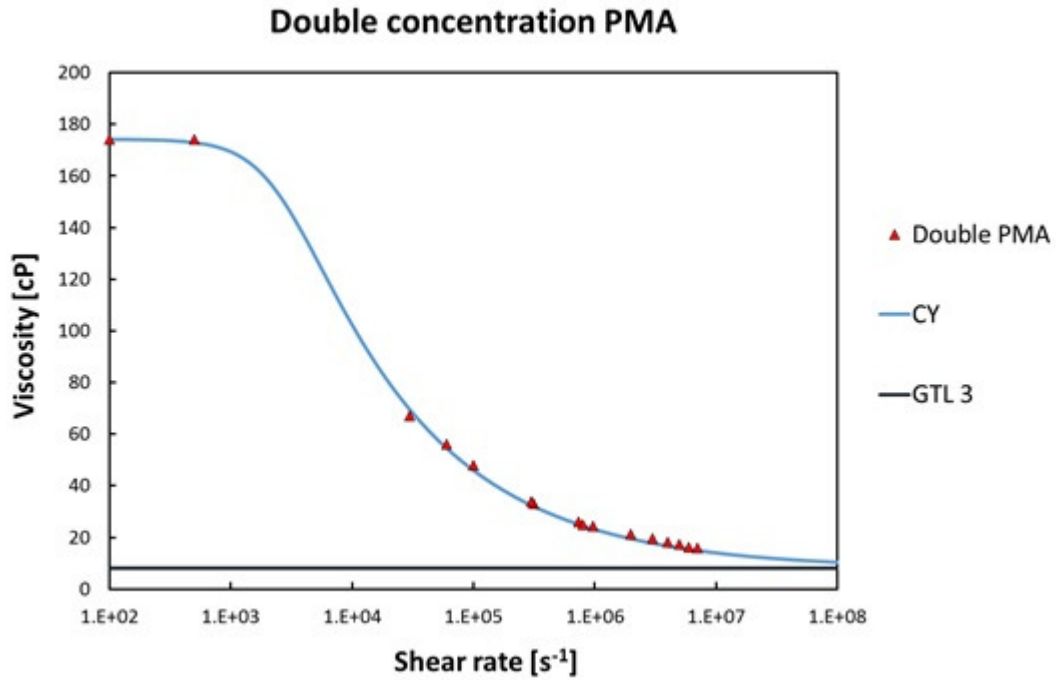


Fig. 7.8: 28%wt PMA in GTL3, Carreau Yasuda fit

Table 7.3 lists the Carreau-Yasuda parameters from fitted curves to the respective experimental data of the gear oil viscosity modifiers.

Table 7.3: CY parameters, gear oil VMs

	η_0 (cP)	η base (cP)	A (s)	n	a
14% PMA	39.04	7.97	5E-05	0.62	1.5
28% PMA	174.2	7.97	4E-04	0.6	2

7.2 HYDRODYNAMIC FILM THICKNESS RESULTS

All hydrodynamic film thickness results shown are obtained for a PMMA disc steel ball contact at a contact load of 10 N.

7.2.1 MODEL POLYMER VISCOSITY MODIFIERS

Initially, model polystyrene viscosity modifiers were chosen for this study so that phthalate esters were necessary to dissolve the viscosity modifiers. However, the

phthalate esters washed off the coating on the polymer discs so no film thickness data were obtainable with polystyrene solutions and the focus shifted to alternative viscosity modifiers.

Figure 7.9 shows the film thickness for pure rolling and at 190% SRR for 3%wt PIP in squalane, the flow curve of which is found in figure 7.4, as well as for neat squalane and the expected film thickness from the zero shear viscosity. No shear thinning effects on film thickness are visible in this solution. Compared to the flow curve in figure 7.4 this suggests a shear rate of below 10^6 s^{-1} in the inlet.

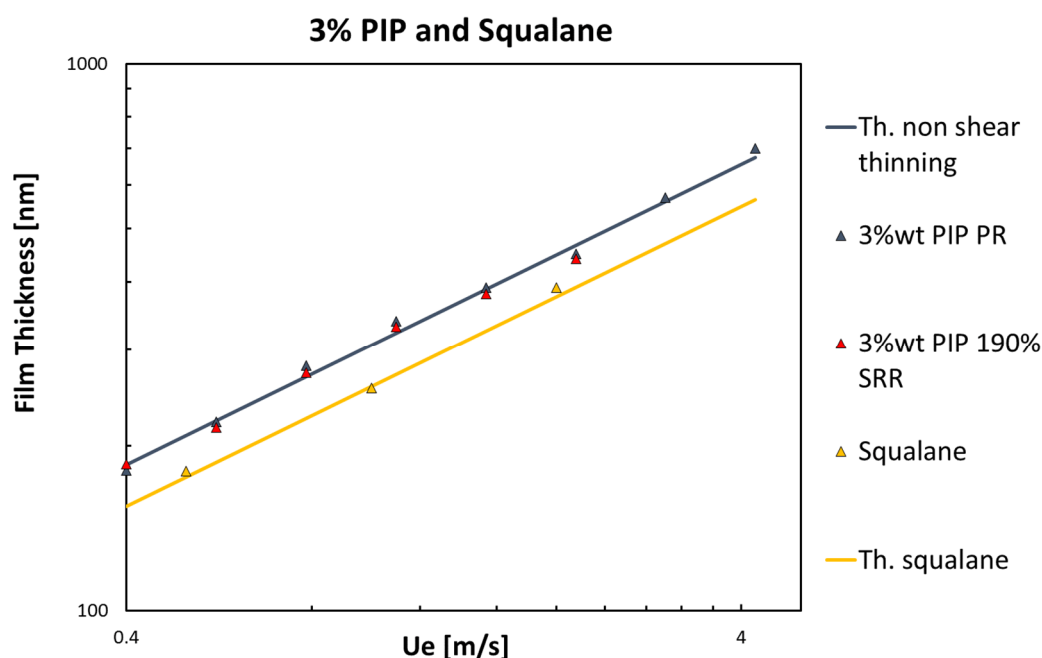


Fig. 7.9: Film thickness versus entrainment speed for 3%wt PIP in squalane, pure rolling and 190% SRR and squalane

7.2.2 ENGINE OIL VISCOSITY MODIFIERS

The three engine oil viscosity modifier blends, HSD di-block, HSD star and OCP featured in figure 7.5 were tested for film thickness as shown in figure 7.10 for pure rolling conditions. Also present in the figure are the equivalent low shear viscosity of the blends, which corresponds to GTL8 and the viscosity of the neat base oil GTL4 in which the VMs were diluted.

A considerable amount of shear thinning is observed. The film thickness for each VM blend is close to that of the pure base oil. Figure 7.5 shows that the three blends shear thin in similar manner and figure 7.10 shows that, while shear thinning at the inlet of the contact in pure rolling conditions, they produce similar films under the same contact conditions.

Also interesting to note is that the slope against entrainment speed for these nearly completely shear thinned blends corresponds closely to the slopes of Newtonian oils. OCP gives a slightly higher film thickness than the HSD polymers. Thus OCP is studied in more detail.

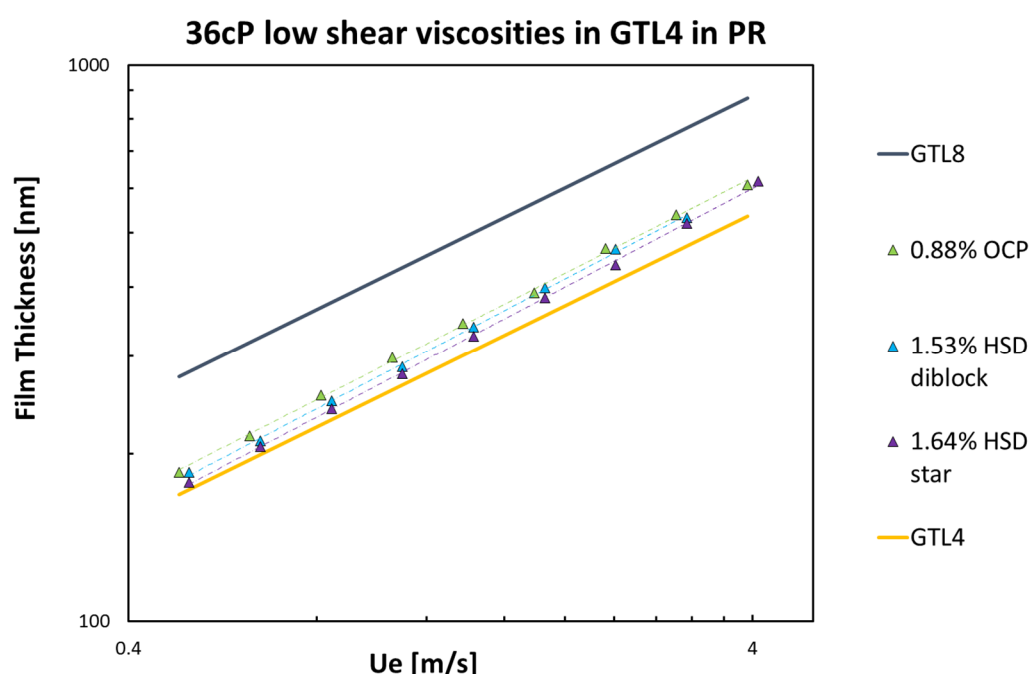


Fig. 7.10: Film thickness in pure rolling for OCP, HSD diblock, HSD star in GTL4

Figure 7.11 shows the same OCP blend data as well as the same blend at 150% SRR. A slight further decrease in film thickness is noted for the high slide-to-roll ratio.

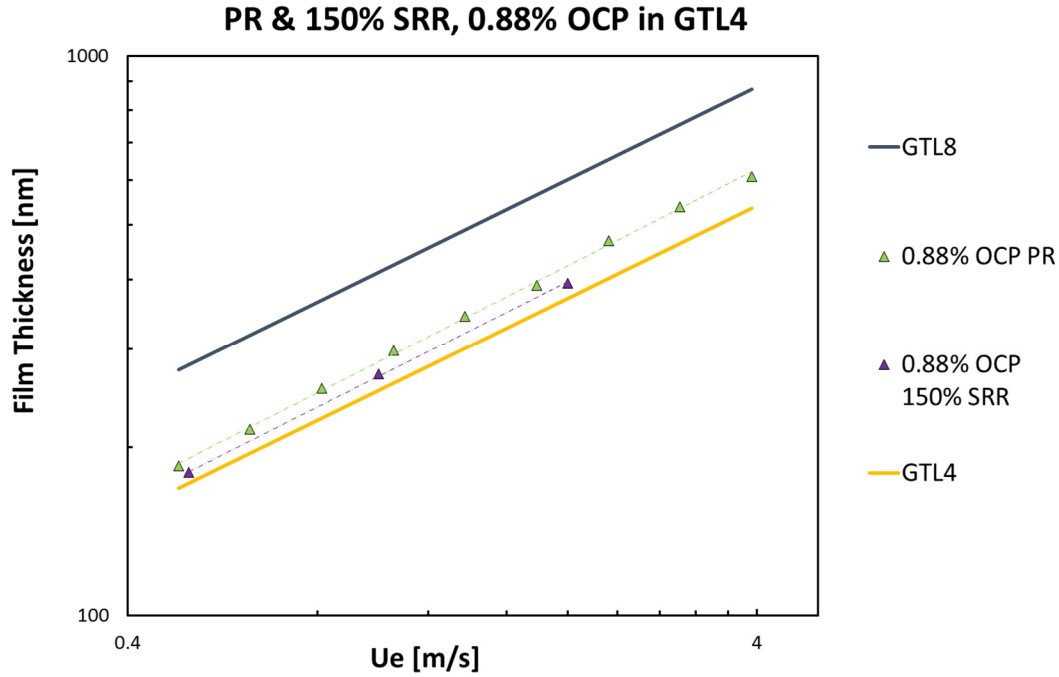


Fig. 7.11: Film thickness versus entrainment speed for 0.88%wt OCP in GTL4; pure rolling (PR) and 150% SRR

In order to investigate the effect of SRR on shear thinning in more detail, a higher concentration OCP solution is tested. Figure 7.12 displays film thickness results at different SRRs for a 5x higher concentration OCP-GTL4 blend, the flow curve of which is shown in figure 7.6. It also features the theoretical film thickness obtained by the low shear viscosity and Eq. 5.23 in Chapter 5, as well as that of the pure base oil.

At the tested conditions the blend shear thins significantly in the contact inlet and the extent of shear thinning increases with SRR. This higher concentration blend does not shear thin down to as close to its base oil as the lower concentration blend. However, it is interesting to note a much smaller slope in $\log(\text{film thickness})$ versus $\log(\text{entrainment speed})$. This indicates that shear thinning is increasing as entrainment speed increases which implies that the effective shear rate in the inlet, that increases with entrainment speed, matches the steep shear thinning part of the flow curve. Achieving this smaller slope is how shear thinning may be implemented in order to effectively reduce friction.

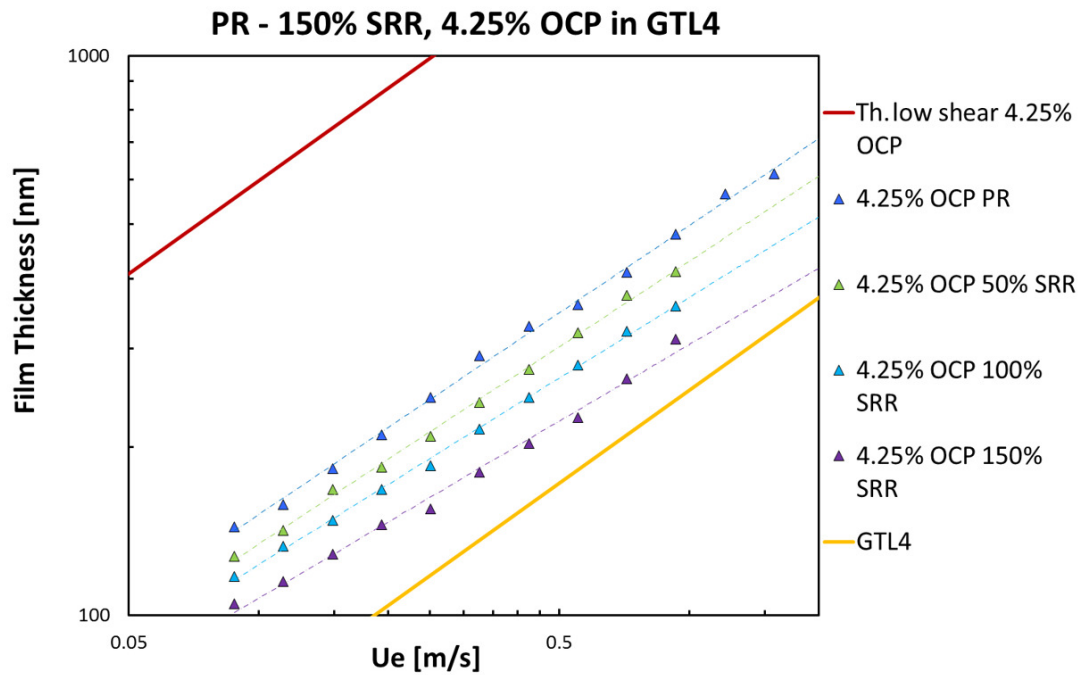


Fig. 7.12: Film thickness versus entrainment speed for high concentration OCP in GTL4; effect of SRR

7.2.3 GEAR OIL VISCOSITY MODIFIERS

Figure 7.13 shows the film thickness for a shear thinning PMA/GTL3 gear oil blend in pure rolling and at 150% SRR. This blend has a similar low shear viscosity to GTL8, though it was not as well matched as the three engine oil viscosity modifier blends and thus features a low shear viscosity nearly 10% higher than GTL8. The reference base oils GTL8 and base oil GTL3 are also plotted in figure 7.13. The flow curve may be found in figure 7.7.

Again a significant amount of shear thinning is obtained, though slightly less than the engine oil viscosity modifiers. The film thickness/entrainment speed slope is similar to the slope of Newtonian oils.

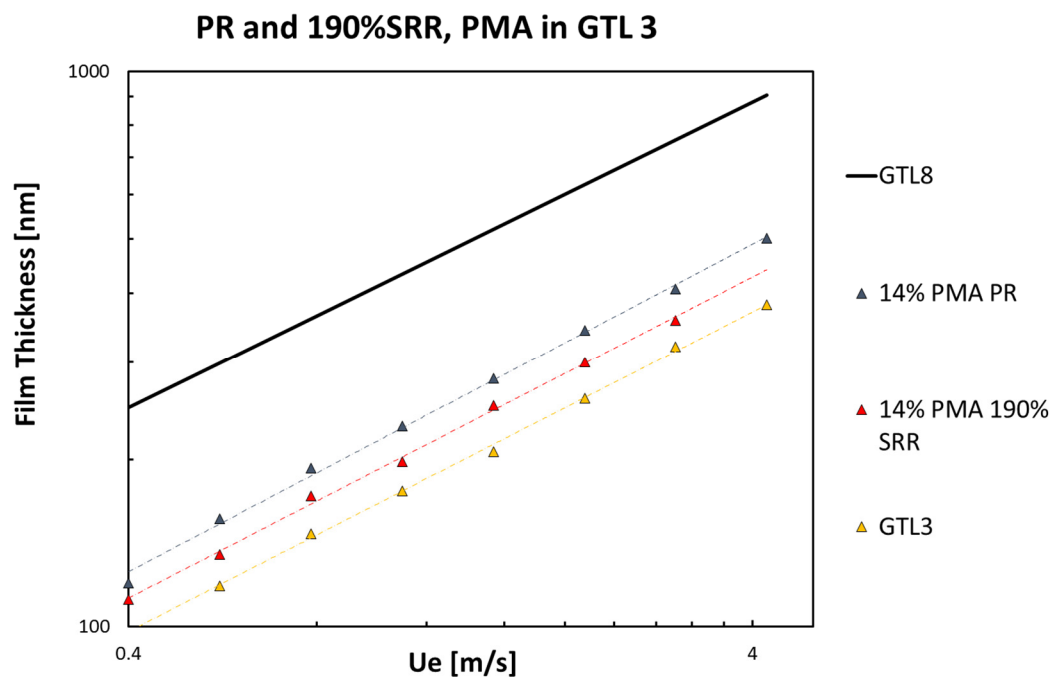


Fig. 7.13: Film thickness versus entrainment speed for 14%wt PMA in GTL3; effect of SRR

Figure 7.14 shows the film thickness results for a similar blend but with double the PMA concentration. The theoretical low shear viscosity film thickness and the base oil are featured as well as various SRRs. The flow curve is presented in figure 7.8.

Again at this higher concentration a smaller slope than that of Newtonian oils is obtained, indicating the increase in shear rate and thus reduction in viscosity with entrainment speed. Furthermore, it appears that as the blend shear thins towards the base oil (i.e. with increase of SRR), the film thickness to entrainment speed slope increases, indicating that the blend is approaching its second Newtonian plateau.

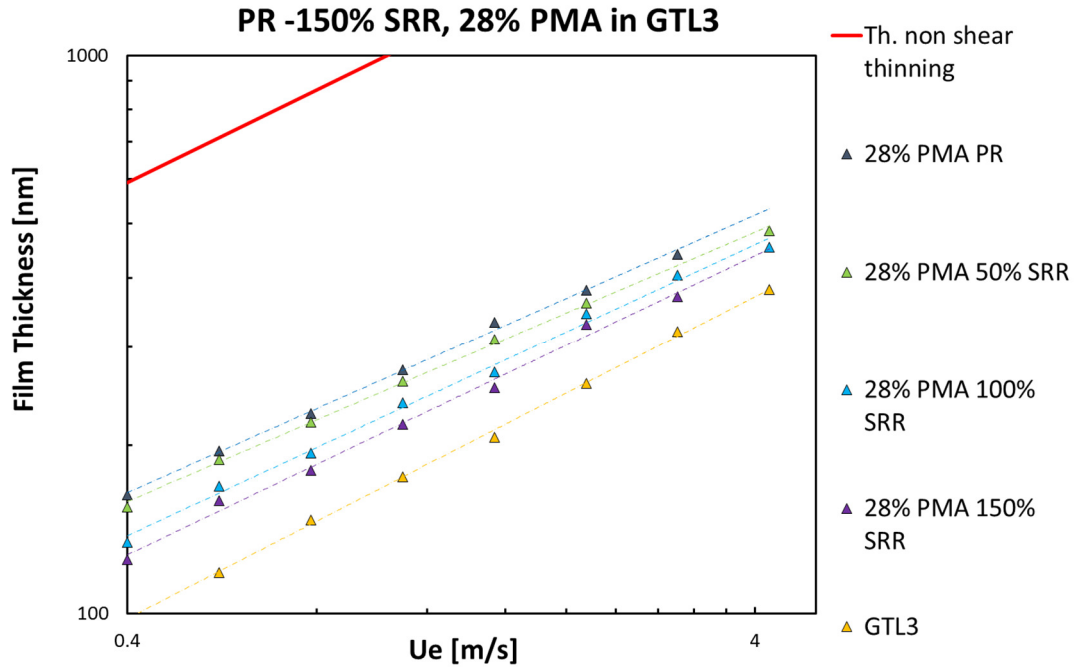


Fig. 7.14: 28%wt PMA in GTL3; effect of SRR

7.3 HYDRODYNAMIC FRICTION RESULTS: FRICTION CURVES

Given the difficulties of obtaining accurate in-contact hydrodynamic friction as described in Chapter 6, only a few representative results on shear thinning hydrodynamic friction are shown. All friction tests presented in this chapter are obtained for a PMMA disc on steel ball contact at a load of 10 N.

Even though phthalate esters could not be used in film thickness tests due to coating removal, they could still be used for friction tests.

Figures 7.15 and 7.16 show a 10%wt 50k g/Mol PS in DEHP blend and a 2%wt 200k g/Mol PS in DEHP blend at an entrainment speed of 2m/s. Also present in these figures are experimental results under the same conditions of base oil (DEHP) and PAOs with the same low shear rate viscosities as the two polymer solutions. Flow curves for these polymer solutions are shown in figures 7.1-3.

For Newtonian oils, the COF varies linearly with SRR. However for shear thinning oils the COF appears to curve as SRR is increased, indicating a reduction in friction compared to Newtonian oils. Furthermore, for both blends, friction is lower than friction of the equivalent low shear viscosity PAO. For the lower molecular weight polymer blend, which shear thins less easily as shown in figure 7.1, the COF reduction is smaller than for the higher molecular weight polymer. For the 200k g/Mol PS the COF tends towards that of the low viscosity base oil.

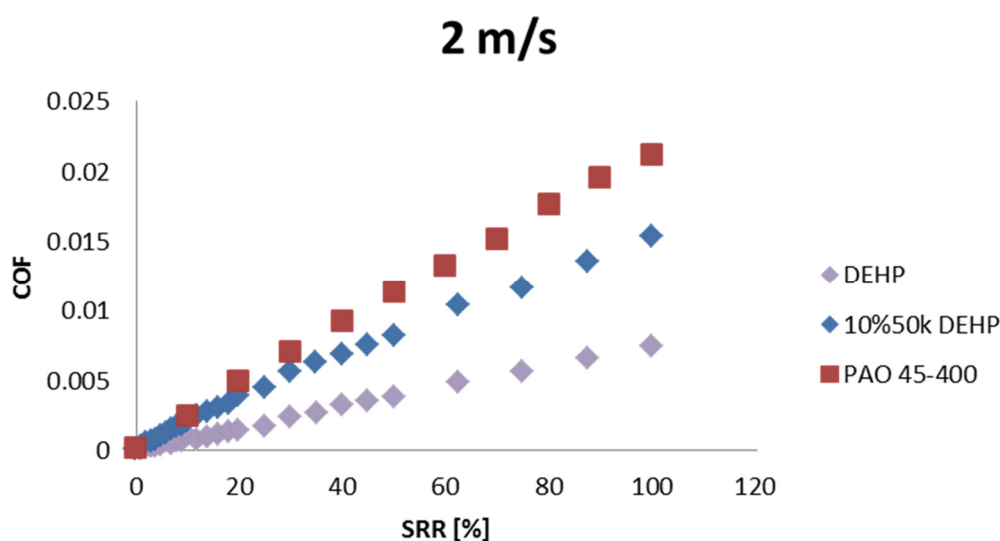


Fig. 7.15: Coefficient of friction versus SRR at $U_e = 2$ m/s for 10%wt 50k g/Mol PS in DEHP, DEHP and PAO45-400 blend

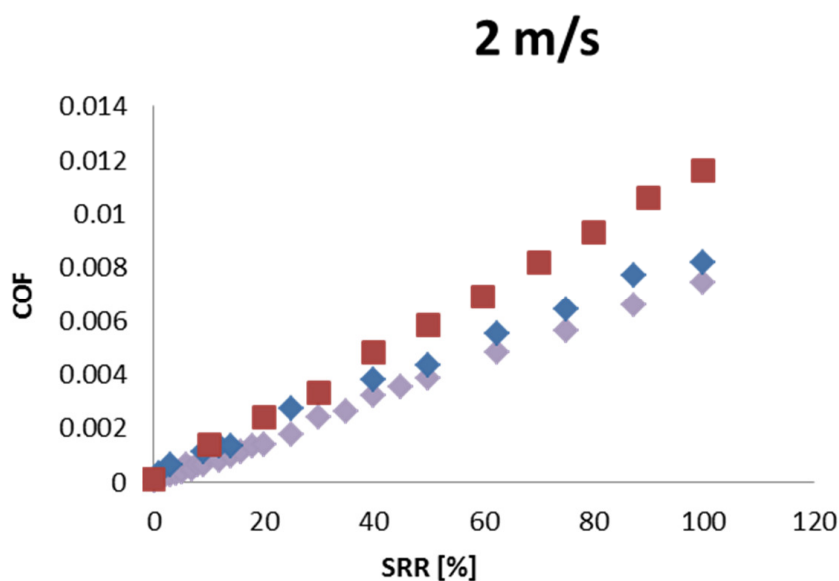


Fig. 7.16: Coefficient of friction versus SRR at $U_e = 2$ m/s for 2%wt 200k g/Mol PS in DEHP, DEHP and PAO10

Figure 7.17 shows the 10%wt 50k g/Mol PS in DEHP blend at different entrainment speeds. As entrainment speed is increased, COF increases, but the shear thinning curvature also increases.

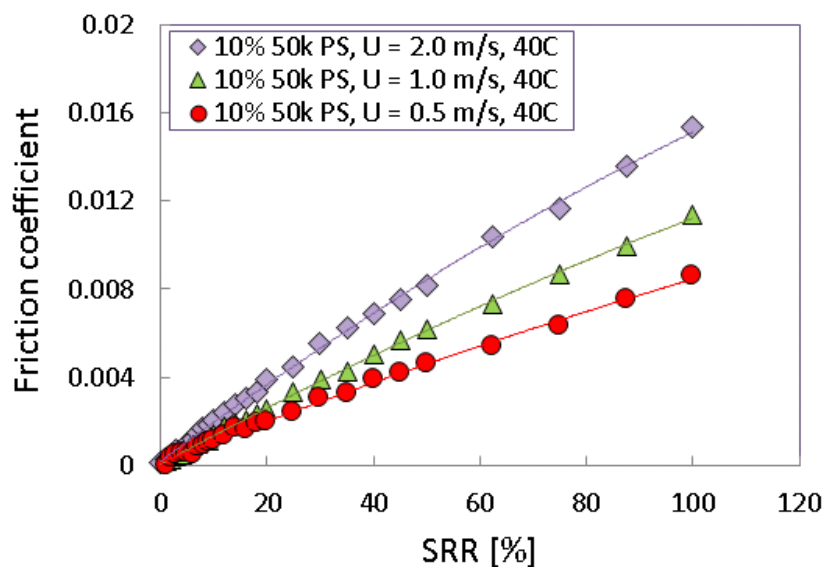


Fig. 7.17: Effect of entrainment speed on coefficient of friction versus SRR for a 50k PS diluted at 10%wt in DEHP

Figure 7.18 illustrates COF against SRR obtained from 0.88%wt OCP in GTL4 at entrainment speeds of 0.5m/s, 1m/s and 2m/s. The curvature is not as strong as for the 50k g/Mol PS in DEHP blend because the OCP blend is of much higher molecular weight and thus has nearly shear thinned to the base oil as is the case for the 200k PS-DEHP blend.

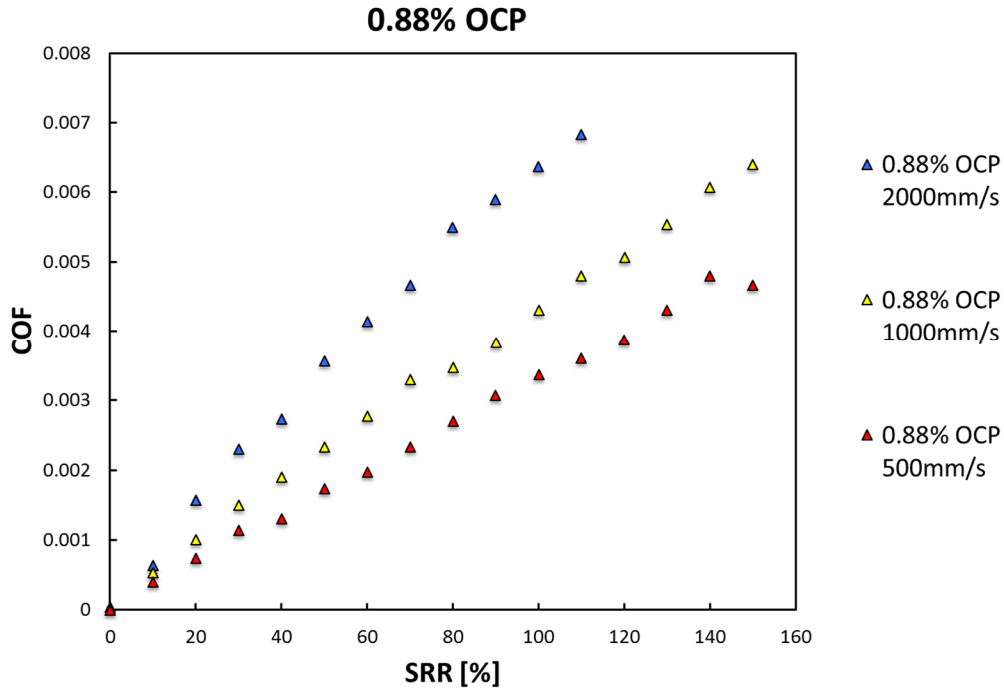


Fig. 7.18: Coefficient of friction versus SRR at $U_e = 2$ m/s for 0.88%wt OCP in GTL4; effect of SRR and entrainment speed

7.4 HYDRODYNAMIC FRICTION RESULTS: STRIBECK CURVES

The conventional Stribeck curve is implemented in pure sliding conditions, i.e. at a SRR of 200%. The MTM however does not operate very well in a soft contact at 200% SRR. Nevertheless it is possible to maintain a constant SRR and increase the sliding speed by increasing the entrainment speed.

Figures 7.19 and 7.20 show such Stribeck curves excluding the viscosity factor in the abscissa at 50% SRR and 100% SRR respectively for a 10% wt. 50k PS in DEHP and two Newtonian oils equivalent to its two Newtonian plateaus. Figure 7.21 shows the Stribeck curve excluding the viscosity factor in the abscissa at 100% SRR for a 0.88% wt. OCP in GTL 4 as well as two oils equivalent to its two Newtonian plateaus.

Also present in figure 7.21 is the Stribeck like curve at 100% SRR of 4.25% wt. OCP in GTL4. In Figures 7.19-7.21 linear trend lines have been added for the Newtonian oils.

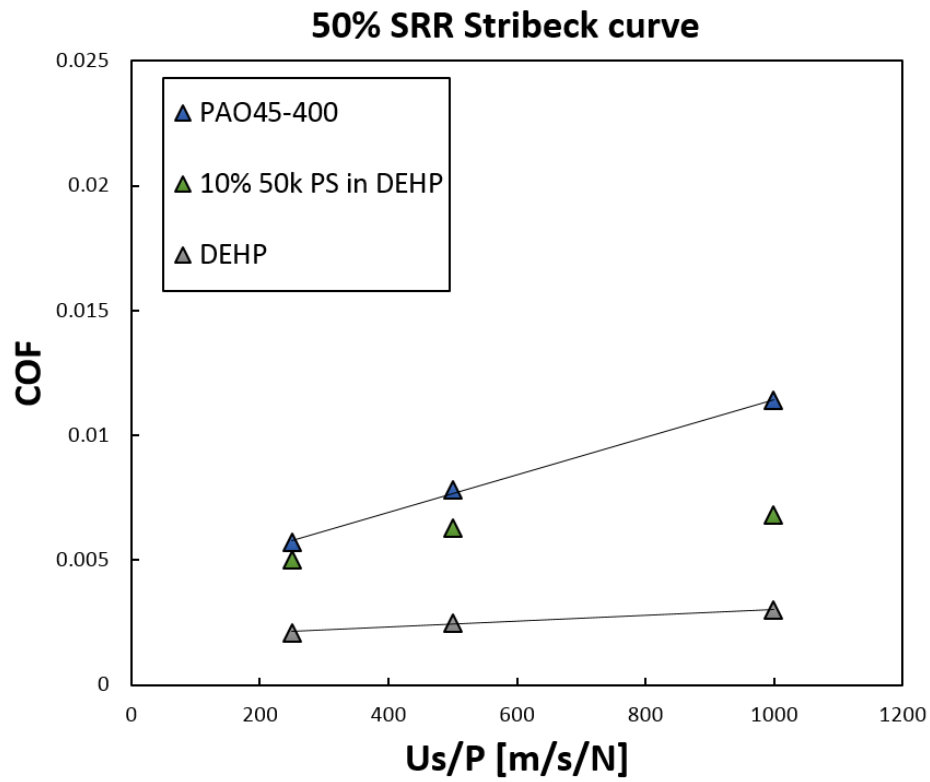


Fig. 7.19: 50% SRR Stribeck like curve of 10% wt. 50k PS in DEHP at 40°C

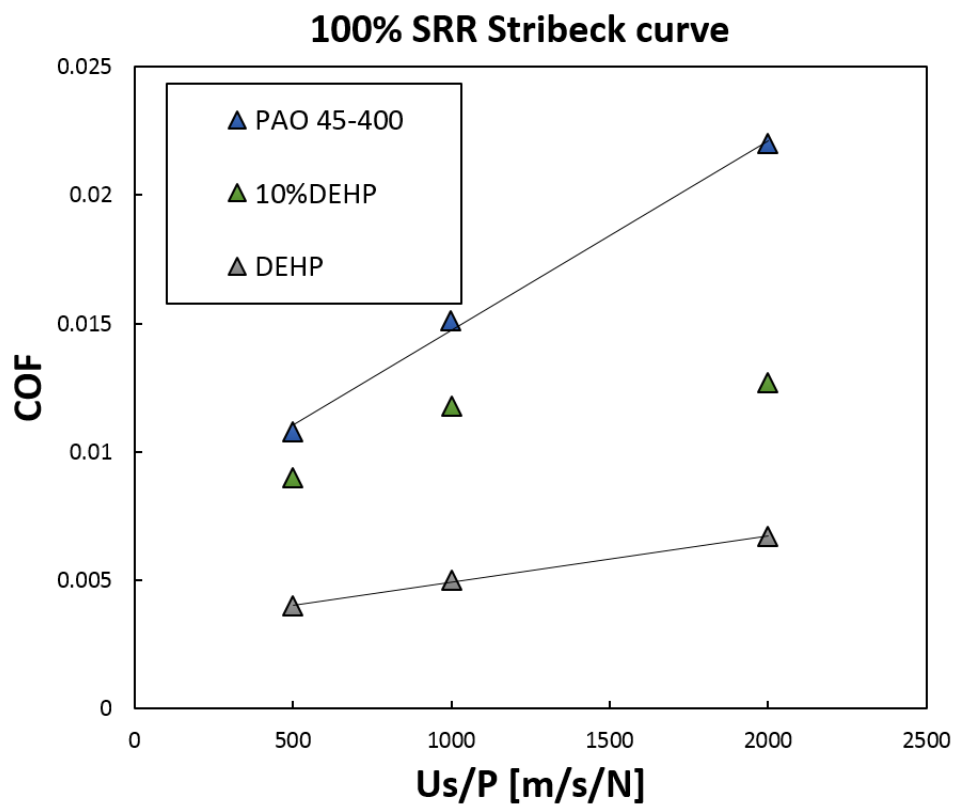


Fig. 7.20: 100% SRR Stribeck like curve of 10% wt. 50k PS in DEHP at 40°C

It is remarkable how first of all less friction is obtained for the shear thinning oil than the PAO mixture of a viscosity equivalent to the first Newtonian, and secondly how an increase in sliding speed amplifies the friction reduction, thus leading to a curvature similar to the predicted curvature in figure 1.2 in Chapter 1.

For the 0.88% wt. OCP in GTL4 blend in figure 7.21 the oil shear thins to the base oil while the higher concentrated 4.25%wt. OCP blend also shows a slight curvature versus sliding speed.

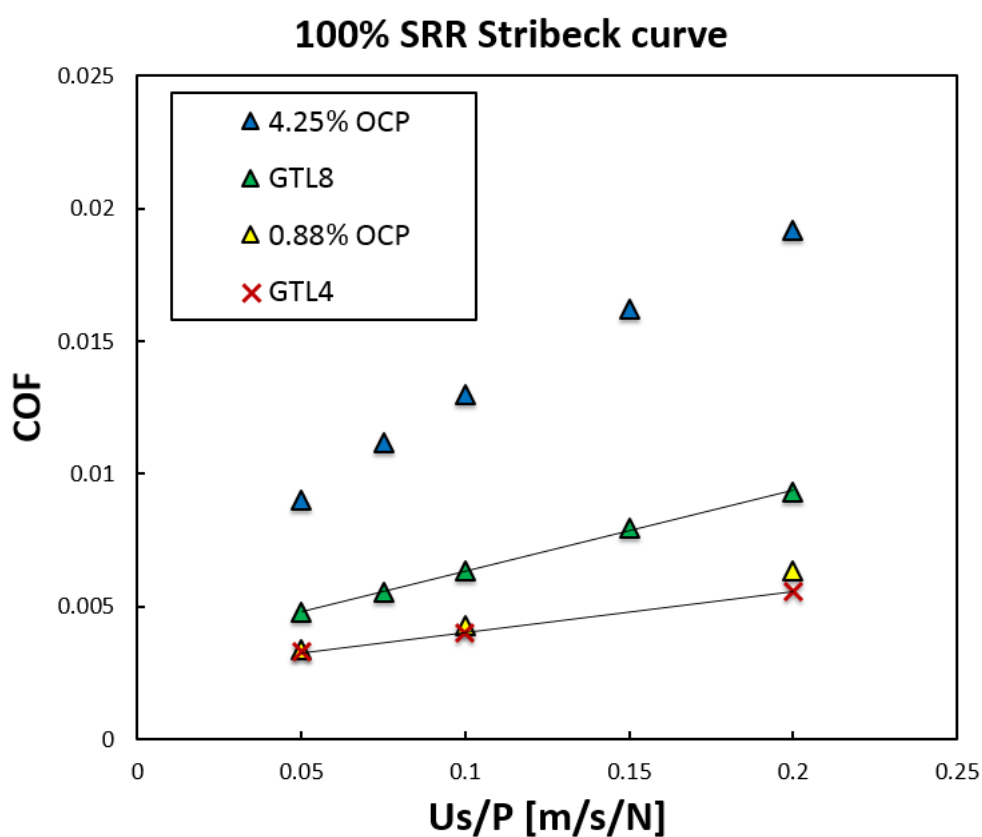


Fig. 7.21: 100% SRR Stribeck like curve of 0.88% and 4.25% wt. OCP in GTL4 at 40°C

7.5 SUMMARY OF RESULTS

- Flow curves are acquired implementing the SVM 3000, A rheometer, a mid shear USV extension and a USV.
- Different amounts of shear thinning may be visualised depending on viscosity modifier type and concentration.
- At the highest shear rates and thus at the highest shear stresses, the viscosity of each blend approaches the viscosity of the respective base oil.
- Due to the viscosity dependency on contact conditions, film thickness and friction reduce according to the shear stress applied in the contact.
- Stribeck like curves implementing a constant SRR are obtainable.
- For this type of Stribeck curve excluding the viscosity factor in the abscissa Newtonian oils show the linear hydrodynamic behavior and shear thinning oils show a curvature as suggested in figure 1.2 in Chapter 1.

8 Discussion

With the overlap of experimental conditions from Chapter 7 it is now possible to compare theory to experiment. Film thickness appears complicated to predict for shear thinning oils due to the difficulty of defining the inlet conditions for a ball on disc setup. However, using film thickness measurements and flow curves, it is possible to predict shear thinning hydrodynamic friction with good accuracy.

It is now important to evaluate the amount of shear thinning based on contact conditions. In order to be able to predict shear thinning it is necessary to attempt to predict first film thickness of shear thinning oils and then friction of shear thinning oils, since friction is dependent on film thickness.

8.1 THEORETICAL AND CALCULATED ANALYSIS OF FILM THICKNESS

It is straightforward to understand and evaluate the shear gradient between two surfaces moving at a velocity difference to each other, at least so long as no shear localisation occurs. It is less straightforward to understand how the oil shear thins at the inlet of contact under pure rolling conditions.

Figure 8.1 shows a schematic of the investigated hydrodynamic contact.

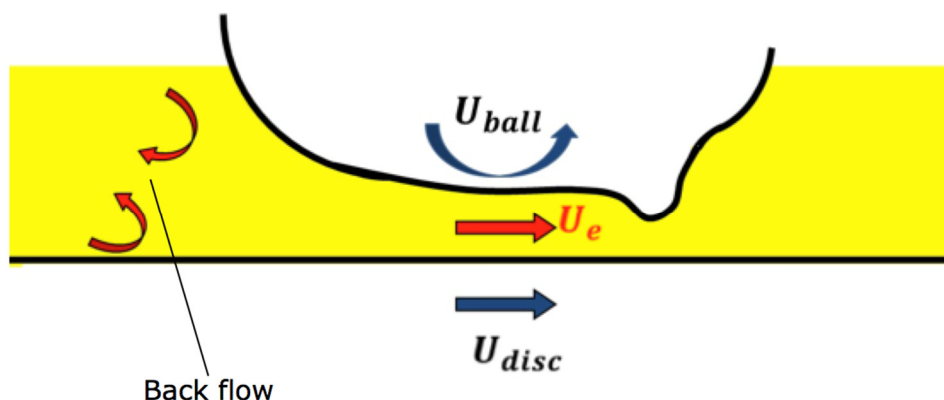


Fig. 8.1: Backflow

From this it can be seen that even when entrainment speed equals the speeds of the two rubbing surfaces, a backflow is created because not all oil is able to be entrained into the contact. It is the high strain rate produced by this backflow that generates shear in pure rolling. The positioning of the applied shear is at the inlet of the contact. However, viscosity at the inlet of the contact governs film thickness. Consequently, if the oil is sheared at the inlet, viscosity drops and so does film thickness, even under pure rolling conditions.

Dyson [1] predicted the maximum shear rate at the inlet of the contact for a hard ball on disc contact in pure rolling as shown in Eq. 8.1.

$$\dot{\gamma}_{inlet}(PR) = \frac{3}{2} \frac{U_e}{h_c} \quad (8.1)$$

where h_c is the central film thickness and U_e the entrainment speed. If a slide to roll ratio is introduced, the backflow is changed and a velocity difference between the rubbing surfaces at the inlet also induces shear. Dyson [1] also obtained a predictive equation for the introduction of a finite SRR (Eq. 8.2):

$$\dot{\gamma}_{inlet}(SRR) = \frac{(3 + \frac{SRR}{2})^2}{6} \frac{U_e}{h_c} \quad (8.2)$$

When $SRR=0$, Eq. 8.2 reduces to Eq. 8.1.

Eq. 8.2 may be applied to the experiments conducted in a soft ball on disc contact. Given the amount of experimental data, and the established film thickness law for soft contacts from Eq. 5.23 in Chapter 5 there is another way of determining the shear rate at the inlet of the contact. Eq. 5.23 from Chapter 5 may be rearranged to Eq. 8.3:

$$\eta_{inlet} = \frac{E'R'_x}{U_e} \times \left(\frac{h_c}{2.7\bar{R}\left(\frac{W}{E'R'_x}\right)^{\left(0.75 \times \frac{8}{3} - 2\right)}} \right)^{1/(2-2 \times 0.725)} \quad (8.3)$$

In this case $R'_x = R$.

The CY equation may be rearranged to Eq. 8.4

$$\dot{\gamma}_{inlet} = \frac{1}{A} \left(\left(\frac{\eta_{inlet} - \eta_{base}}{\eta_0 - \eta_{base}} \right)^{\frac{a}{n-1}} - 1 \right)^{1/a} \quad (8.4)$$

All input values for Eq. 8.3 and 8.4 are experimentally obtained.

Figure 8.2 shows the shear rates obtained for Dyson's predictions (Eq. 8.2) applied to the experimental setup using the experimentally obtained central film thickness of the 4.25%wt OCP/GTL4 blend. Values at two entrainment speeds are shown. Also present in figure 8.2 is the shear rate obtained from the experimentally-measured film thickness via a combination of Eq. 8.3 and Eq. 8.4.

Dyson's shear rate predictions are directionally consistent with the values obtained from experimental film thickness in that they increase with SRR. However, they are almost an order of magnitude lower at low SRR.

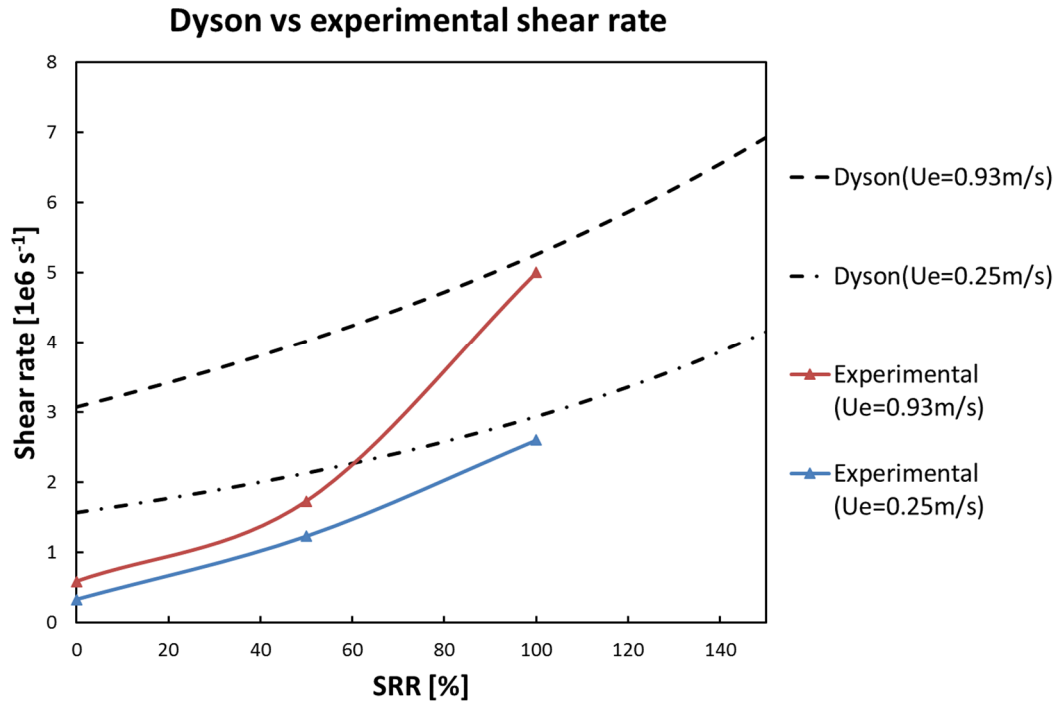


Fig. 8.2: Dyson predictions of and experimental evaluations shear rates, 4.25%wt OCP in GTL4

Figure 8.2 is limited by the number of combinations of U_e and SRR studied. Figures 8.3 and 8.4 show the variation of film thickness with entrainment speed plotted with a linear film thickness axis rather than the more commonly used logarithmic one. At a given entrainment speed, film thickness decreases approximately linearly with SRR for a given test oil. This means that it is possible to interpolate linearly to obtain film thickness at all intermediate SRRs.

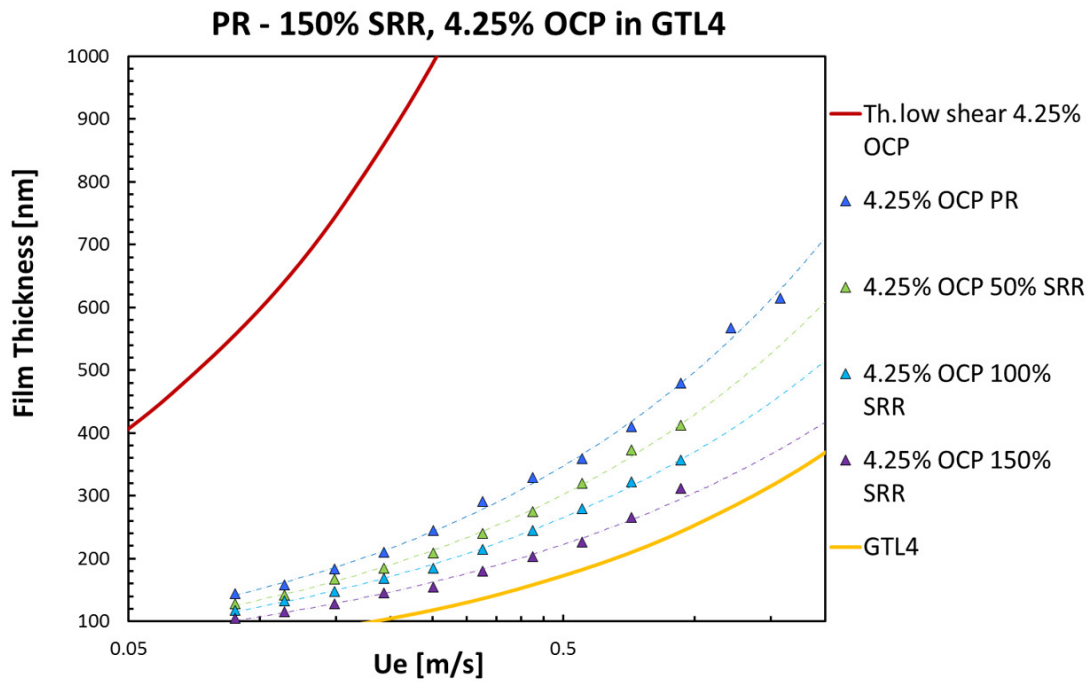


Fig. 8.3: Figure 7.12 shown with linear film thickness axis

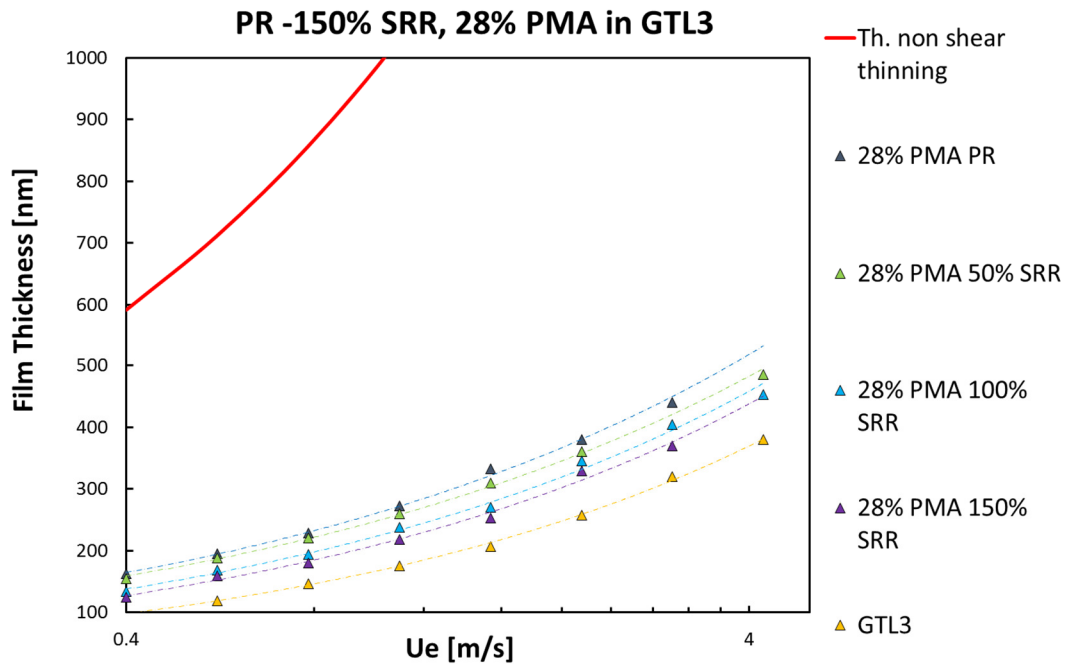


Fig. 8.4: Figure 7.14 shown with linear film thickness axis

Figures 8.5-8 show Dyson's predicted inlet shear rates from Eq. 8.2 compared with values calculated from experimental film thicknesses for 4.25%wt OCP, 0.88%wt

OCP, 28%wt PMA and 14%wt PMA respectively at entrainment speeds 0.5m/s, 1m/s and 2m/s. In these results film thicknesses have been interpolated from measured ones. Again it can be seen quite clearly that for pure rolling conditions and medium to low SRR Dyson's predictions capture the correct order of magnitude. At higher SRR however, the shear rate values obtained from measured film thicknesses deviate significantly from Dyson's shear rate predictions.

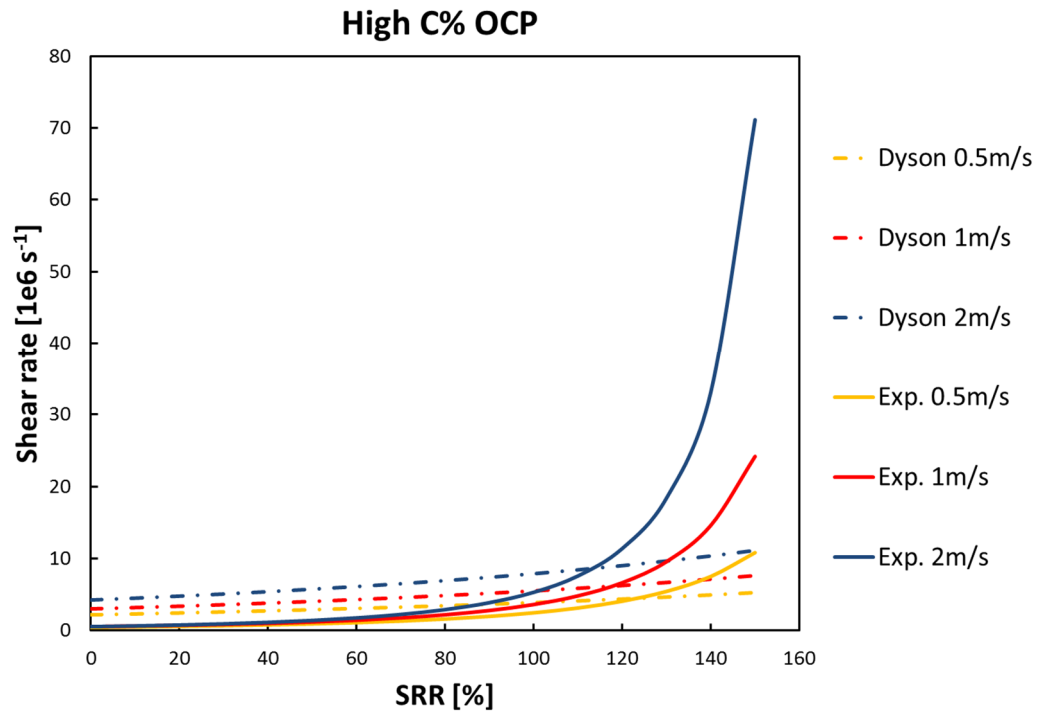


Fig. 8.5: Comparison of inlet shear rates based on film thickness measurements with those predicted by Dyson; 4.25%wt OCP in GTL4

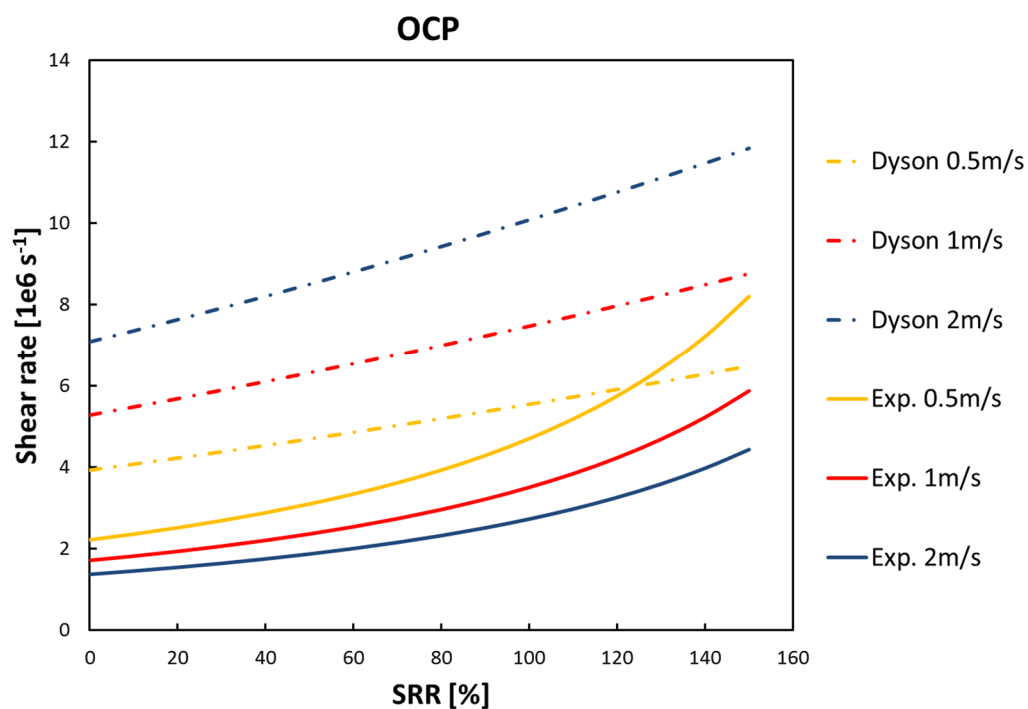


Fig. 8.6: Comparison of inlet shear rates based on film thickness measurements with those predicted by Dyson; 0.88%wt OCP in GTL4

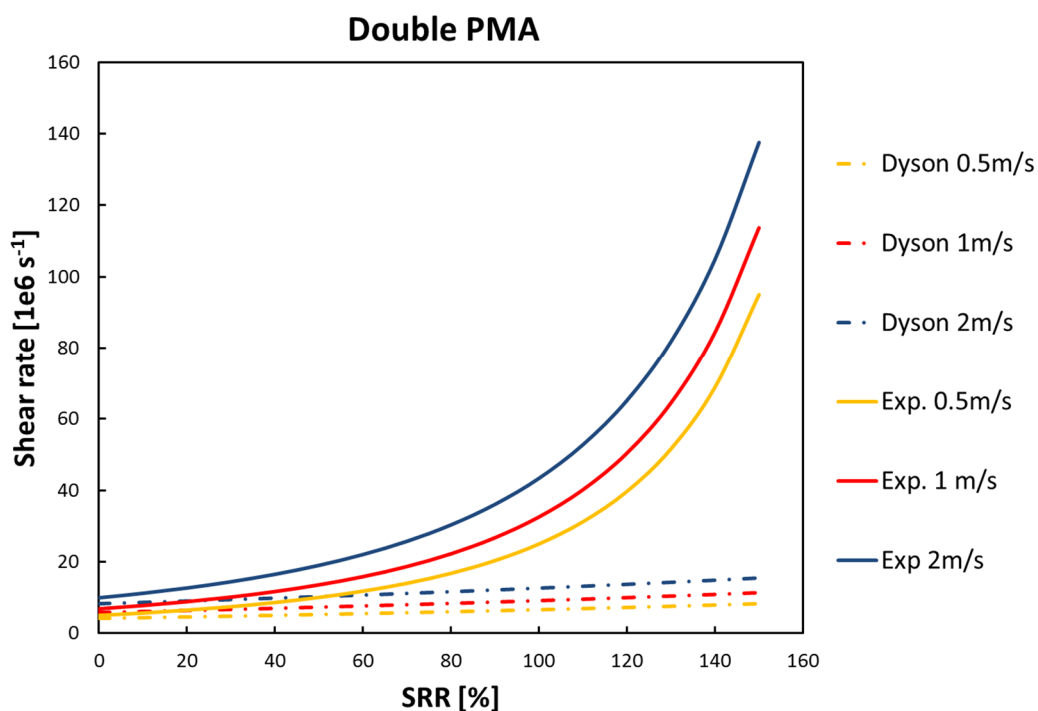


Fig. 8.7: Comparison of inlet shear rates based on film thickness measurements with those predicted by Dyson; 28%wt PMA in GTL3

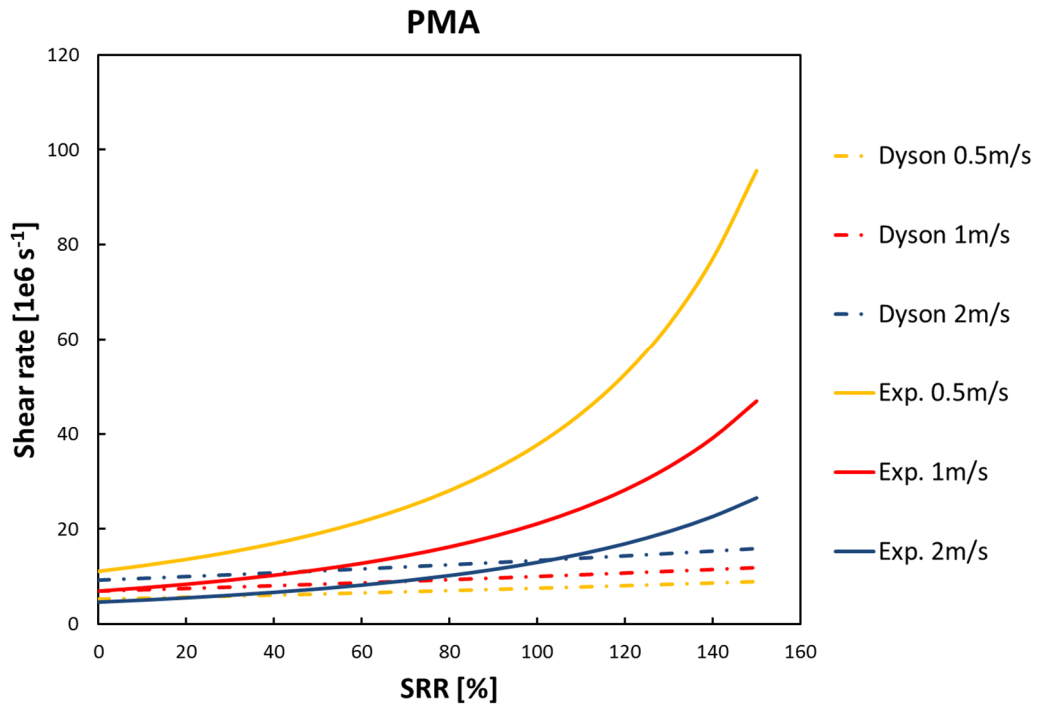


Fig. 8.8: Comparison of inlet shear rates based on film thickness measurements with those predicted by Dyson; 14%wt PMA in GTL3

It is surprising to note that at low polymer concentration (figures 8. 6 and 8.8) based on film thickness measurements, inlet shear rate decreases as entrainment speed increases. This originates from the fact that the measured film thickness versus entrainment speed curves for these fluids are almost the same as for the Newtonian oils.

8.2 THEORETICAL AND CALCULATED ANALYSIS OF FRICTION

Figure 8.9 presents a shear stress versus strain rate curve obtained by the method described in Chapter 6 including the discussed correction factor of 1/1.8.

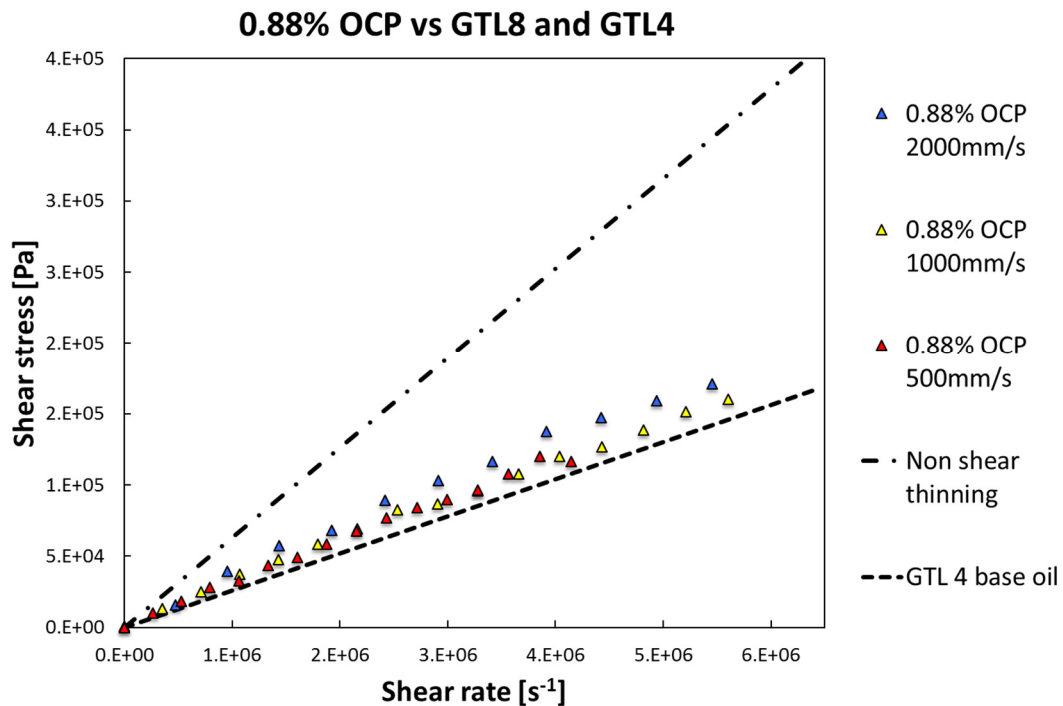


Fig. 8.9: Stress strain curve for 0.88%wt OCP in GTL4 for different entrainment speeds

For treatment of film thickness as described in the previous section, it can be assumed that piezoviscous effects in the inlet are negligible. This is because the pressure in the contact inlet does not exceed 10 MPa. Hence, the Carreau-Yasuda equation relating viscosity to strain rate at atmospheric pressure can be used. However, hydrodynamic friction originates from within the centre of the contact where the mean pressure reaches about 45 MPa. This produces a small but still significant piezoviscous effect. Thus a realistic pressure viscosity coefficient of 14 GPa^{-1} will result in a doubling of viscosity at 45 MPa. Because shear thinning results from shear stress rather than strain rate this increase in viscosity has to be taken account of in terms of its effect on shear thinning.

It is however possible to modify the flow curves against shear rate to produce flow curve against shear stress by implementing Eq. 8.5.

$$\tau = \dot{\gamma} \times \eta(\dot{\gamma}) \quad (8.5)$$

Thus the flow curve of 0.88%wt OCP in GTL4 from figure 7.5 becomes figure 8.10. The Carreau-Yasuda equation can be modified to fit such data by replacing shear rate by shear stress and changing the CY constants.

$$\eta_{atm} = \eta_{base} + (\eta_0 - \eta_{base}) \times \left(1 + (A'\tau)^{a'}\right)^{(n'-1)/a'} \quad (8.6)$$

It should be noted that n' , a' and A' are different from n , a and A from the CY equation and are presented in table 8.1.

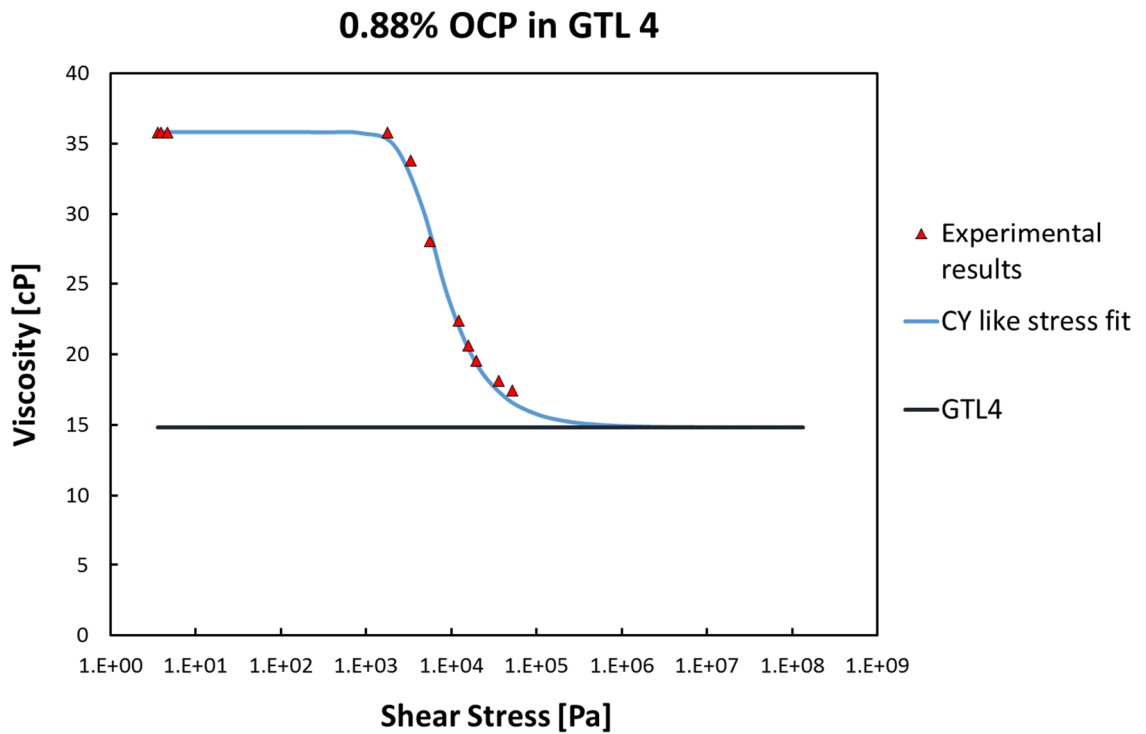


Fig. 8.10: Viscosity against stress plot with a theoretical fit implementing Eq. 8.6

Table 8.1: Parameters for Eq. 8.6

	η_0 (cP)	η base (cP)	A' (s)	n'	a'
0.88% OCP	35.8	14.8	2.5E-04	0.037	3

In order to apply this to the ball on polymer disc contact, an iterative approach is applied. First the conventional CY equation is used to determine the mean in-contact viscosity from the strain rate, assuming atmospheric pressure conditions. This mean viscosity is then used to determine the mean shear stress within the contact using Eq. 8.7.

$$\tau = \dot{\gamma} \times \eta_{atm}(\dot{\gamma}) \times e^{\alpha \bar{P}} \quad (8.7)$$

This calculated mean shear stress is then applied in Eq. 8.6 to determine the mean in-contact viscosity, allowing for both shear thinning and piezoviscous effects. These last two steps (Eq. 8.7 and 8.6) are then applied iteratively to convergence – normally just 2 iterations.

Figure 8.11 compares the converged prediction at 1 m/s entrainment speed with the experimental results. An accurate match is obtained between experiment and theory.

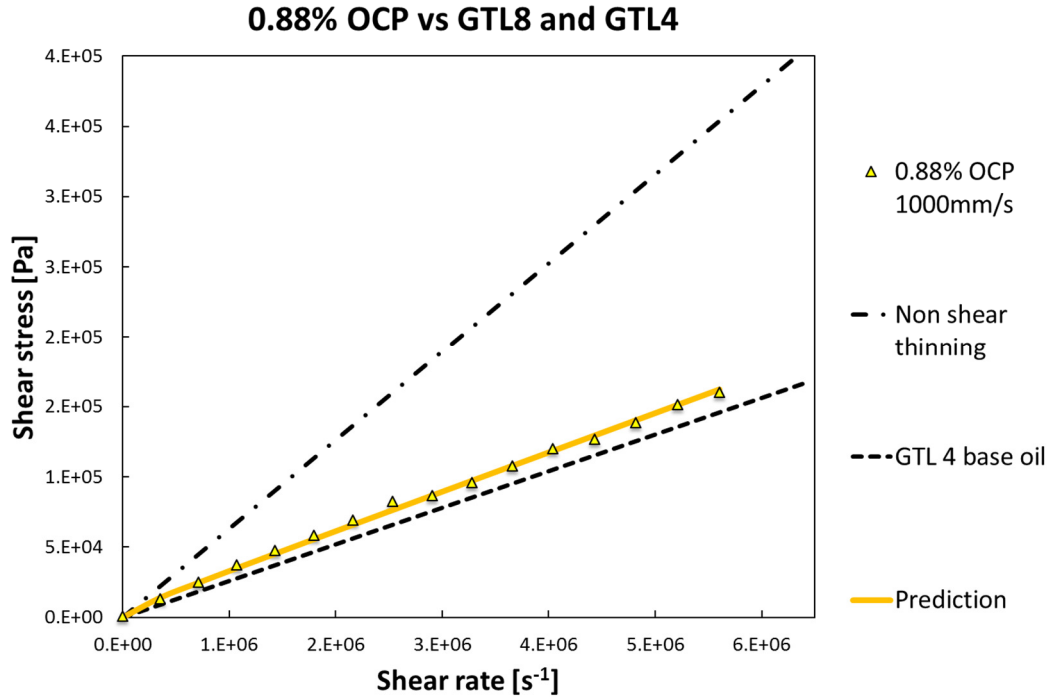


Fig. 8.11: Stress strain prediction and experimental results for 1m/s entrainment speed

8.3 CONCLUSIONS

This chapter has combined the calculations of flow curves with film thickness and friction measurements in soft EHL polymer disc on steel ball contacts to explore the impact of VM shear thinning on friction and film thickness. For film thickness measurements, shear stress at the inlet of the contact appears great enough to nearly shear thin the polymer-containing oils to their base oil viscosity and consequently produce films only slightly greater than those of the base oil. This may be understood from Figure 8.12 which shows representatively the inlet shear thinning positioning on the flow curve of the shear thinning oils. At low concentration, the oil shear thins nearly to the base oil. For the high concentration blends of the same polymer, the oil does not shear thin to the base oil but still reduces significantly in viscosity. The polymeric viscosity modifiers investigated are of too high molecular weight for the model contact and thus have shear thinned beyond the steep shear thinning range that is beneficial to friction reduction. In order to better understand the shear induced film thickness reduction it would thus be helpful to investigate lower molecular weighted polymer

blends that still shear thin significantly, but see the steep part of their flow curve in the shear rate range at which the soft ball on disc contact operates.

Since shear thinning is more directly linked to shear stress than to shear rate it becomes complicated to associate a shear rate to the inlet of the contact. Not only do the rubbing surfaces induce a shear but also is a viscometric backflow inducing a significant proportion of the shear. This backflow could probably be simulated by fluid dynamics, however it is most likely viscosity dependent. Thus perhaps an inlet shear stress might be more representative of the contact than Dyson's inlet shear rate.

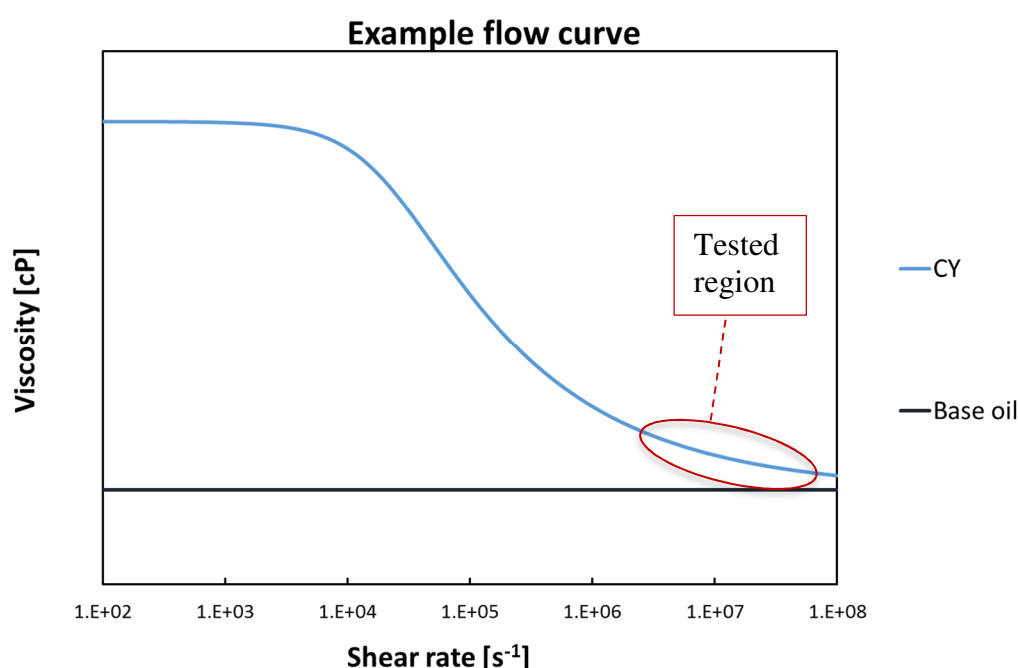


Fig. 8.12: Shear rates in the contact visualised on the flow curve

For friction, good agreement may be found between experiment and theory, after allowing for piezoviscous effects to be calculated and after introducing a scaling factor. The technique appears thus quite powerful; however, it is necessary to understand the origins of the scaling factor in order to introduce this technique in hydrodynamic lubrication research. The author is hopeful that future work may solve this issue.

In the model contact, the friction reduction originates from two shear thinning phenomena. In the Hertzian contact region the rubbing surfaces induce a shear which reduces the viscosity in the contact to reduce hydrodynamic friction. Furthermore, the shear thinning at the inlet of the surfaces of the contact reduces the central film thickness. This then increases the shear rate in the centre of the contact and subsequently the shear stress, having as a result a further reduction in viscosity in the Hertzian contact area. Hence hydrodynamic friction is further reduced by the shear thinning film thickness.

It is obvious that too much film thickness reduction due to shear thinning would become detrimental to the contact; thus it will always be necessary to have a minimal Newtonian base oil viscosity beyond which the oil is unable to shear thin for conforming contacts in order to avoid, for example, scuffing in the journal bearings. In practice, the base oil viscosity is limited by other components in the engine which work in the elastohydrodynamic regime, as those contact conditions allow even base oils to shear thin.

Lubrication of the inlet of a journal bearing is however different from the model contact used in this study. Instead of generating a backflow, side leakage is promoted. Since reduction in film thickness due to shear thinning has an important effect on hydrodynamic friction, it could become important to understand how the inlet shear in a journal bearing is obtained from the bearing's geometry, the lubricant's properties and the running conditions. Thus the next step in order to be able to design an oil to reduce friction *via* shear thinning is to apply the work presented in this thesis to an actual journal bearing. This will then allow to optimise the oil design from a flow curve for journal bearings. Finally the limitations provided from other components in the engine require consideration in order to optimise engine efficiency *via* polymer shear thinning. In the ideal case, a lot of temporary shear thinning would occur while permanent shear thinning remains limited. However, it is equally important to have the steep part of the flow curve at the operating regime of the engine in order to maximise performance increase.

This can be seen in the modified Stribeck curves of figures 7.19 and 7.20. The 50k g/mol PS is an ideal shear thinning VM for the soft compliant ball on disc contact.

Friction is reduced over a Newtonian oil and the reduction is amplified with increased sliding speed. Thus the blend improves lubrication efficiency by adapting intelligently to the contact conditions.

Typical engine oil viscosity modifiers are of much higher molecular weight. The OCP example in figure 7.21 shows only little adaptability for a high concentrated blend and no adaptability for the low concentrated blend. This is because the shear stress is very high in the model compliant ball on disc contact and most of the viscosity thickening of the VM is shear thinned or, in the case of the lower concentrated OCP blend, all of the VM is completely shear thinned.

In practice the engine needs mapping out in terms of shear stress. Then shear thinning of different VM types and different molecular weights can be measured. According to the literature as discussed in Chapter 3.5 (figure 3.7) different concentrates (up to a limiting concentration) and base oil blends should not affect the shear thinning behavior when SSI is plotted against shear stress. Finally, the type of VM and molecular weight which overlaps its rapid onset of shear thinning with the engine regime and which shows the most shear thinning can be chosen. The base oil viscosity and concentration of VM would be iterated in order to limit the amount of shear thinning before wear occurs. According to the literature on several oils tested, as discussed in Chapter 3.8, the limit is at an HTHS of about 2.4cP, however perhaps the method suggested here to look at complete flow curves rather than one single HTHS value and to design the flow curve around the engine will allow the reduction of the HTHS further than 2.4cP and thus improve engine efficiency beyond today's standards.

References

- [1] Dyson, A., Wilson, A.R.: Film thicknesses in elastohydrodynamic lubrication by silicone fluids. Proceedings of the Institution of Mechanical Engineers 180, pp.97–112, (1965–66)

9 Conclusions and future work

9.1 CHAPTER BY CHAPTER SUMMARY OF THE THESIS

Chapter 1 puts into perspective the potential of designing an engine oil to shear thin in order to improve engine efficiency. The general approach implemented in this thesis in order to prove the concept of improving engine efficiency via polymer shear thinning is outlined.

A review of published work on viscosity modifiers, their shear thinning behavior and the effects they may have on engine lubrication has been conducted in Chapters 2 and 3.

A thorough study of the viscosity modifier solutions is employed in Chapter 4, including GPC to show the molecular weight distribution and flow curves to quantify shear thinning. Temperature-viscosity data show the mechanical properties of the lubricants. The chapter also describes the successful development of a model compliant ball on disc contact. This contact avoids piezoviscous effects in the contact inlet and minimizes piezoviscous effects in the Hertzian contact area.

For the first time flow curves covering a large range of shear rates are obtained accurately for both model and commercial polymer solutions. Innovative techniques have been implemented in order to achieve this, such as new calibration methods, the development of new mid-shear viscometers and methods to avoid permanent shear thinning being included within the measured temporary shear thinning flow curves.

The Carreau-Yasuda equation may be applied to fit this shear thinning data. A good fit is obtained, although it should be noted that the number of fitting parameters available in this equation allow it to fit most types of data that transition between a high and a low value.

As described in Chapter 5, two techniques have been developed in order to measure film thickness in soft EHL (isoviscous-elastic regime).

Hart and Hidrovo's double dye fluorescent film thickness for measuring technique has been developed in-situ for the model contact [1-3]. For this technique, an innovative ultra-low runout platform was developed as well as an inverted microscope which was fitted on to a CETR tribometer.

An interferometry technique for plastic soft contacts has also been developed (for Young's moduli > 1 GPa; coated PDMS was pioneered unsuccessfully with this method due to its too low Young's modulus). This is the first time that conventional normal incidence interferometry has been applied to soft EHL. It shows several advantages over the fluorescent double dye technique, including much greater precision and ease of use.

The main existing isoviscous-elastic film thickness equations have been tested using this new optical interferometry application. Although existing equations predict film thickness reasonably well (within 5 to 30% depending on entrainment speed), they are not exact. Instead a new soft contact equation Eq. 5.23 has been developed to fit any Newtonian oil under the range of conditions studied. This theoretical equation was successfully tested in this study on three different types of soft contact: steel ball on PMMA disc, steel ball on PU disc and steel ball on PC disc.

In Chapter 6 the development of a novel method of measuring hydrodynamic friction is outlined, based on a mini traction machine with a lubricated steel ball on polymer disc contact. It is found that, unlike the behaviour seen in high pressure EHL contacts, coefficient of friction is proportional to SRR and varies with entrainment speed for Newtonian oils. It is possible to deduce stress strain curves from experimental film thickness results and this shows that tests at different entrainment speeds for the same oil all fall on the same stress strain curve.

Unfortunately there is a discrepancy between shear stress calculated from measured friction and that expected from the viscosity for Newtonian oils. This means that friction results and theory require a scaling factor in order to be matched. The model

contact, the mini-traction machine and even a CETR tribometer setup were thoroughly researched in order to understand the origins of this discrepancy. Several obvious possibilities were found not to have any effect. Friction from the meniscus surrounding the contact was found to make a significant contribution, but this was not great enough to be the sole source of the discrepancy. Viscoelastic effects, however, were found to occur.

In order to be able to use the novel friction method in subsequent work, testing conditions were limited to ones at which the scaling factor was constant and the scaling factor was implemented in order to match experiment to theory.

Chapters 7 and 8 combine measured flow curves, film thickness measurements and friction measurements on polymer solutions to explore the impact of shear thinning on hydrodynamic behaviour.

Film thickness was found to be significantly smaller than that predicted from the low shear viscosities of the polymer solutions in hydrodynamic soft contacts, just as found in the literature for hard EHL contacts. The film thickness also decreased with increasing slide-to-roll ratio, unlike for Newtonian oils.

For shear thinning oils, where the inlet strain rate corresponds to the region over which there is a rapid onset of shear thinning in the flow curve, the film thickness slope against entrainment speed is lower than that of Newtonian oils. Implementing this slope as engine oil design parameter may be a way to enhance engine efficiency via shear thinning.

For pure rolling contacts, the reduction of film thickness found in the tests is believed to originate from the high local strain rate resulting from recirculation of oil in the inlet, as explained by Dyson for hard EHL contacts [4]. Dyson's hard contact EHL shear rate theory at the inlet of the contact was found to give correct orders of magnitude for slide-roll ratios below 100% for soft ball on disc contacts. For higher SRR, experimental results diverge significantly from Dyson's predictions.

By testing several oils it was found that it is not possible to designate a universal inlet position for shear thinning oils in order to obtain a shear rate and thus predict film thickness. This is not surprising as the oil viscosity varies strongly across the inlet.

Hydrodynamic friction was successfully measured for shear thinning oils using the soft contact method. Instead of showing linear behaviour of coefficient of friction (COF) against SRR as for the Newtonian oils, the COF appears to curve below linearity due to shear thinning and even reaches the base oil COF for the most severe cases. Different entrainment speeds however appear to overlap in a stress strain curve.

By implementing experimental film thickness results, the scaling factor of $1/1.8$ on the stress strain curve, experimental flow curve results, a new Carreau-Yasuda-like equation fit to a viscosity-stress curve and the experimentally obtained film thickness equation for soft contacts, it is possible to predict hydrodynamic friction for shear thinning lubricants with good accuracy.

Shear thinning oils improve hydrodynamic efficiency and thus engine efficiency in the modified Stribeck curve as initially suggested in Chapter 1.

9.2 MAIN CONCLUSIONS ARISING FROM THIS WORK

Viscosity modifiers thicken a base oil and improve the viscosity index when comparing the blend to a Newtonian oil of equivalent viscosity and similar chemistry as the base oil of the blend.

All of this viscosity thickening may be lost due to temporary shear thinning. Shear thinning is shear stress dependent. In an engine, higher shear stress yields to higher, undesirable friction. However, by shear thinning due to the stress applied in the engine the overall stress or friction experienced in a lubricated contact in the engine is reduced. In fact, the more the shear stress, the more the viscosity reduces so the more the engine oil adapts to the engine conditions in order to reduce friction.

An engine operates in various lubricant shear stress conditions depending on the varying speed and power at which it is run. Wide variation in shear stress also occurs due to the number of components a single engine oil has to lubricate. Thus an adaptable, shear thinning oil is highly beneficial to engine efficiency.

This adaptable phenomenon is illustrated in the modified Stribeck curves, theoretically in figure 1.2, or experimentally in figures 7.19 and 7.20.

Viscosity modifiers have a range of shear stresses over which they shear thin. The range depends on molecular weight and type of the viscosity modifier.

It is crucial to have an overlap between this shear thinning shear stress range and the shear stress range applied in the contact over which one wishes to produce an adaptive engine oil.

As illustrated in figure 7.21, the 0.88% wt. concentrated OCP engine oil blend shear thins to the base oil and thus the oil behaves as its base oil under practical conditions and so is non adaptive. The shear stress experienced in the chosen tribological contact is above the shear thinning shear stress range of the OCP VM.

It should be noted that this type of oil still could be beneficial to a larger system if it also lubricates other highly loaded components under low shear stress, since for these conditions the VM will thicken the oil and reduce mixed and boundary friction.

Friction reduction comes from a multiplied phenomenon: first shear thinning at the inlet of the contact reduces film thickness, then the film thickness reduction yields to an increase in shear rate in the centre of the contact, and finally this further increase in shear rate causes the oil in the centre of the contact to shear thin further, which reduces friction further.

9.3 SUGGESTIONS FOR FUTURE WORK IMPLEMENTING THE METHODS OF THIS THESIS

The author would like to highlight three areas where future work might build on and advance the current work presented in this thesis.

- (a) Friction discrepancy
- (b) Predicting film thickness for shear thinning lubricants
- (b) Choice of VM

9.3.1 THE FRICTION DISCREPANCY

The new method for measuring friction in soft EHL by using plastic discs developed in this study is very easy to use and potentially very powerful. Unfortunately its usefulness is currently limited by the fact that there is a discrepancy between the values measured and those predicted from simple hydrodynamic theory for Newtonian oils. Despite considerable efforts the origins of this discrepancy were not fully identified. This should be a priority in future work. The origins may be revealed by a study of a wider range of viscosity oils and polymer elastic Young's moduli. However the development of a reliable soft-EHL model may also help reveal the origins by quantifying the in-contact and out-of-contact friction values more reliably than is currently possible. The possible presence of viscoelastic effects also needs greater consideration and study.

9.3.2 PREDICTING FILM THICKNESS FOR SHEAR THINNING LUBRICANTS

The optical method developed in the current project is very powerful and a great improvement on previous methods for measuring film thickness. It shows that the shape of the contact can vary, possibly due to shear thinning in the inlet. To explore this further and make the most of the new optical method a soft-EHL model is needed that incorporates both shear thinning and the disc's viscoelastic response.

9.3.3 THE CHOICE OF VM

In hindsight the choice of polymers made in this study produced several important constraints. The model polymers bought off the shelf did not produce the results sought, as the solubility of PS and PIP and the stability of PIP limited their applicability to the techniques developed.

On the other hand the commercial polymers supplied were not very well defined and were very different from one another, making it difficult to carry out systematic investigation. PMA appeared to function well in the various tests, had low dispersivity and dissolved easily in conventional base oils. In future work it is strongly recommended that tests be carried out of a family of such PMAs having different molecular weights. Light scattering and GPC could be applied to these in order to accurately define their molecular weights for a few of these molecules.

By exploring the impact on shear thinning, film thickness and friction of a range of molecular weights and concentrations of such polymers in a series of different viscosity base oils the author believes that our understanding of the impact of shear thinning on lubrication could be considerably improved.

9.4 FUTURE WORK ON VM SOLUTION SHEAR THINNING IMPLEMENTING OTHER METHODS

Measuring hydrodynamic friction in a model soft-EHL contact has proved more complicated than expected. The underlying reason for this is that the in-contact friction is very small, so that out of contact contributions such as the friction from the meniscus and other possible unknown sources of friction become significant. Furthermore, friction measuring equipment is limited in sensitivity and not well suited to measure forces of the order of 0.01 N.

It is therefore suggested to use a reliable journal bearing test rig in order to measure accurately in-contact friction in conditions similar to an engine. This approach has, of course, been quite widely used in the past as discussed in Chapter 4 but has never been

standardized. Preliminary work not described in this thesis has already been carried out by the author on a PCS Instruments journal bearing machine which has been instrumented to measure hydrodynamic friction accurately. A method of measuring film thickness in the rig using ultrasonics has also been designed.

For future work the author believes that a combination of soft EHL and plain journal bearing friction studies with well-defined polymer solutions would be a good way forward.

References

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- [4] Dyson, A., Wilson, A.R.: Film thicknesses in elastohydrodynamic lubrication by silicone fluids. *Proceedings of the Institution of Mechanical Engineers* 180, pp.97-112, (1965-66)

10 Appendices

10.1 USV HIGH PRECISION TESTING MANUAL

Step 1: eliminating sources of contamination

1. Removal of teflon top

The USV Teflon top has two purposes: to stop excess lubricant contaminating the testing chamber and to keep the heat across the stator and rotor as uniform as possible. Tests were conducted at different temperatures. It was found that the absence or presence of the Teflon top did not affect viscosity measurements, indicating that it did not, in practice, influence the test lubricant temperature. Furthermore, removal of the Teflon top greatly reduced the quantity of test lubricant needed; to the extent that it would not contaminate the chamber.

Removing the Teflon top will reduce sources of contamination when using a new oil and enables better control of the following steps since the user is able to visually supervise the amount of excess oil whilst replenishing the contact with lubricant.

2. Removal of the USV cover

This removal is needed in order to remove the flexible plastic pipe from the USV chamber. Put a beaker underneath the chamber outlet pipe to catch exiting oil. When the rotor is travelling vertical during the flush processes, oil will fly out horizontally, thus one can install a sheet of aluminium foil into the beaker standing up vertically in order to catch the sprayed oil and guide it into the beaker. The USV cover is not required during testing, though should be put back on the rig at the latest after test completion in order to protect the internal parts from dust.

3. Clean rotor and stator

For the best results the rotor and stator were dismantled in order to clean them thoroughly between tests. First, wipe off most of the oil with tissue and some solvent. Then place both rotor and stator in a sonicated bath of toluene in a fume cupboard for ten minutes. Dry these with a heat gun, roll up a thin piece of tissue to extract oil and solvent from the heat sensor hole (this is very important, otherwise oil will exit when the stator is reinstalled on the USV and the temperature sensor is inserted. This oil-solvent mixture can contaminate the contact). Then place both rotor and stator in an acetone bath for 10 minutes and repeat the drying process. It is important that the pieces are clean and dry before they enter the acetone or isopropanol bath, with no droplets of toluene left on the surface, otherwise a white residue forms and affects results. Isopropanol may be used as alternative to acetone, though it is not as effective. Be aware that touching the samples with bare hands or blowing at them will dirty them. For optimal results, this washing procedure is required for each new oil or even each new test if the oil shear thins permanently.

4. Rotor and stator assembly

Assemble rotor and stator on the USV as per PCS Instrument's instructions. In order to insert the rotor into the stator, carefully put a few droplets of the oil to be tested onto the rotor. Make sure that the bottom edge of the rotor is fully lubricated and that the rotor is pushed into the stator slowly from the top with small rotational movements in order to avoid the rotor getting trapped inside the stator. For trapped pieces, sonication is useful to allow for dismantling.

Step 2: calibration / setting up the instrument

For calibration to set the viscometer gap, the reference fluid squalane should be measured at different shear rates and temperatures using the test method explained in step 3. Any batch of high purity squalane purchased should have the same viscosity. squalane is suggested as reference oil for any tribological test equipment for this

reason, and because it is commercially available at reasonably low cost, and because the health and safety precautions required for this liquid are minimal.

The user has the choice of measuring the viscosity of the squalane batch with a viscometer of choice, or using the measurements provided in tables 4.2 and 4.4, which are measured to above ASTM standard (error margins of 0.1% - 0.5% depending on temperature).

After the machine is calibrated as per PCS Instruments' user manual, restart dismantling cleaning process in order to run a new test lubricant. It should be noted that dismantling the rotor and stator and re-assembling them does not affect the calibration of the system.

Step 3: effective testing

After rotor and stator have been assembled as per Step 1, the test oil is already inside the contact. Nevertheless a flush procedure will be undertaken in order to ensure first that the complete contact is lubricated and second that minimal excess oil is left on top of the geometry.

1. For the flushing procedure the rotational speed should be reduced from 5000 rpm to 500 rpm since the shear stresses present at 5000 rpm may be high enough to permanently shear thin a VM-containing oil. The temperature may be set to the test temperature.

2. A lot less oil will be used for the flush procedure. Typically a total of 0.1-0.5ml will be used. When the stator moves rotor downwards from the rotor, carefully distribute some microdroplets on to the rotor while manually turning the clutch. Repeat this process every one or two times when the stator moves downwards, depending on how much excess oil is left outside of the contact on top of the stator. The flushing procedure may be cancelled after one or two software flushing steps. The amount of excess oil should be minimal when the flushing procedure is stopped.

3. Enable the temperature compensation technique in the settings and reduce the number of shear cycles to 3. When running two lubricated surfaces against each other at 10^6 - 10^7 s^{-1} in a tribological contact, the oil is subjected to shear heating. This effectively means that the oil sample temperature rises and thus the viscosity drops. In certain applications it is thus difficult to distinguish between shear heating and shear thinning of the oil. It was not until just recently that developers have found ways to produce viscometers that are able to capture viscosities at very high shear rates. PCS Instruments have an innovative approach: a clutch system was developed which engages on a static rotor. The torque applied to the stator is measured during the first hundreds of microseconds of engagement. Thus shear heating of the oil during the measurement is minimised. This process will happen whether the temperature compensation is enabled or disabled. Even though the amount of shear heating is minimised, some minor shear heating effects still occur, typically between 0.1C and 7C depending on shear rate and viscosity of the lubricant.

If the friction is measured the extent of shear heating can be predicted and PCS Instruments have added an option in their software called “temperature compensation”. When this feature is enabled, the USV will add a pre-cycle to each set of engagement cycles (in our case 3 engagement cycles). In the pre-cycle, the clutch will engage at the sought shear rate and temperature and the temperature rise rate will be measured. The temperature of the chamber will then be reduced by a calculated temperature offset. When a shear cycle is now performed, the oil will shear heat precisely to the sought temperature at the instance when the viscosity measurement is taken. This feature is at the peak of its accuracy for temperature offsets between 0.1C and 4C.

5. Testing shear thinning oils:

Most oils that exhibit temporary shear thinning will also permanently shear thin in the USV. In fact some oils which appear to temporary shear thin when running USV shear rate range tests, actually exhibit only permanent shear thinning. It is of utmost importance to be able to distinguish between the two phenomena. Permanent shear thinning can be identified on the USV by repeating a test at a set shear rate several times. The first series of measurements should be taken at the lowest shear stress at which the

USV operates well. This is typically for a viscosity below 10 cP measured at a shear rate of 10^6 s^{-1} . If permanent shear thinning occurs, a linear viscosity decrease should be noticeable across the first few data points (each data point entails a minimum of 4 shear engagements as previously explained). Eventually the viscosity levels out and may even start increasing again (this typically happens after hundreds or thousands of engagements). Should the viscosity decrease linearly of the first few data points, it is then possible to back-extrapolate the linear viscosity line to a zero engagement viscosity. This viscosity corresponds to the temporary shear thinned viscosity. If the oil does not permanently shear thin at 10^6 s^{-1} , a higher shear rate or a lower temperature may be attempted.

Whichever test programme is applied, it is recommended to include a measurement at 10^6 s^{-1} at the beginning of testing and one measurement at 10^6 s^{-1} at the end of testing to verify that no permanent shear thinning has occurred throughout the test.

If the oil has permanently shear thinned, the rotor and stator need to be cleaned and reassembled with fresh oil before further measurements for the highest precision.

However, a more user friendly testing procedure for shear thinning oils which is found to still be very accurate is to only wash the rotor and stator when a new oil is tested. Then one single shear rate is tested with 12 engagements resulting in three average viscosity measurements. This allows to obtain the un-permanently-sheared oil at the given shear rate. Then a flushing procedure is introduced, before the next shear rate is tested.

It is recommended to only test 0.6e6, 1e6, 3e6, 6e6 and 10e6 s^{-1} since this well covers a large part of a logarithmic scaled shear rate axis and suffices to fit the Carreau-Yasuda equation.

It should be noted that the USV's highest precision viscosity measurements is for viscosities between 3 and 20 cP since such an oil will allow the rotor to rotate smoothly through the fluid for a long enough period of time for the torque sensor to capture data. The standard settings of the USV set the rotor to engage for 8 revolutions over which period the torque sensor is programmed to automatically filter the correct data.

10.2 ABANDONED MID SHEAR VISCOMETERS

10.2.1 MID SHEAR RHEOMETER EXTENSION

A Rheometer extension was developed to fit the rotor and the stator of the USV on to the TA Instruments Hybrid Rheometer (see figure 10.1). The stator holder screws into the TA Instruments heated Peltier plate and is radially insulated with a tight-fit Teflon chamber. Alignment is ensured by two coupling pieces attaching the rotor to the rotating head of the Rheometer. An RTD temperature sensor enables accurate reading of the temperature in the stator 5 mm away from the contact. Whereas the rheometer's range of turning speed would allow for shear rates up to $10^6 s^{-1}$, shear heating limits shear rates to $10^5 s^{-1}$. This shear rate is sufficient to bridge the shear rate gap between the results from cone on plate geometry and the USV.

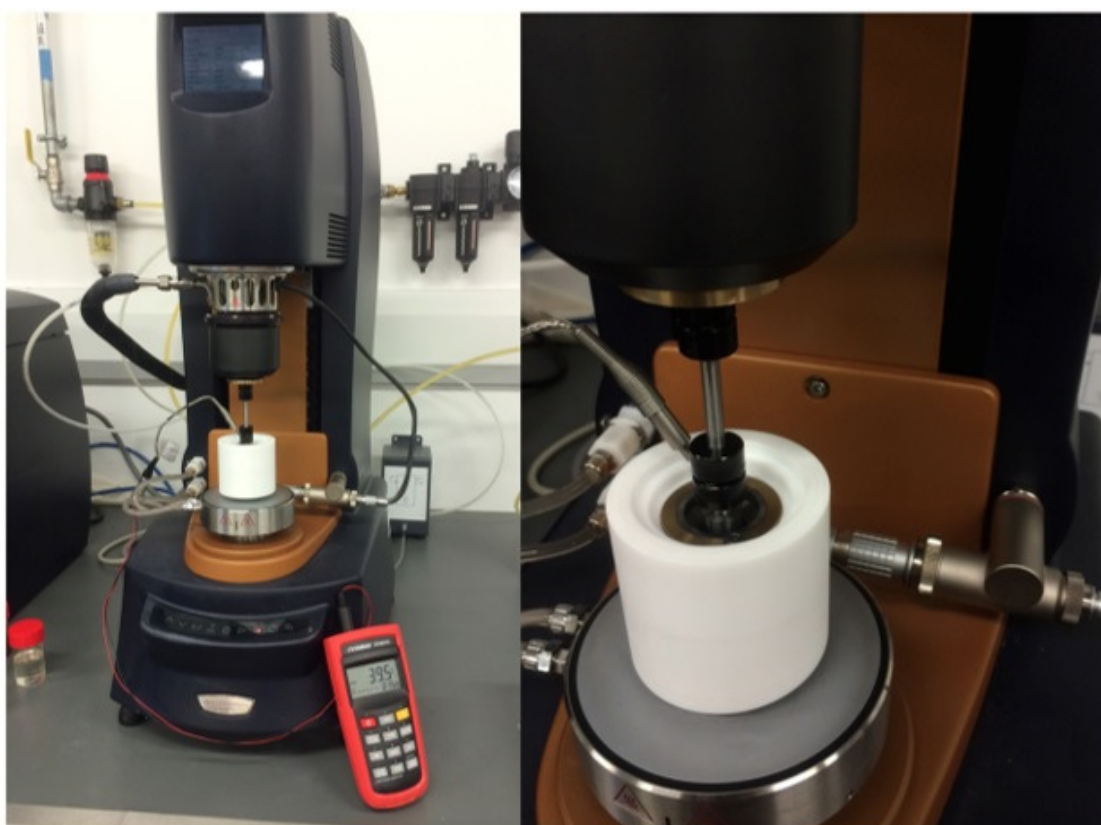


Fig. 10.1: Rheometer mid shear extension

Results on the Newtonian lubricant squalane show a drop in viscosity as the shear rate is increased (see figure 10.2). These results are repeatable and independent of the

speeds set in the test program. It is suspected that the rheometer needs calibrating. According to the SVM the viscosity of squalane is 15.13 cP at 40C.

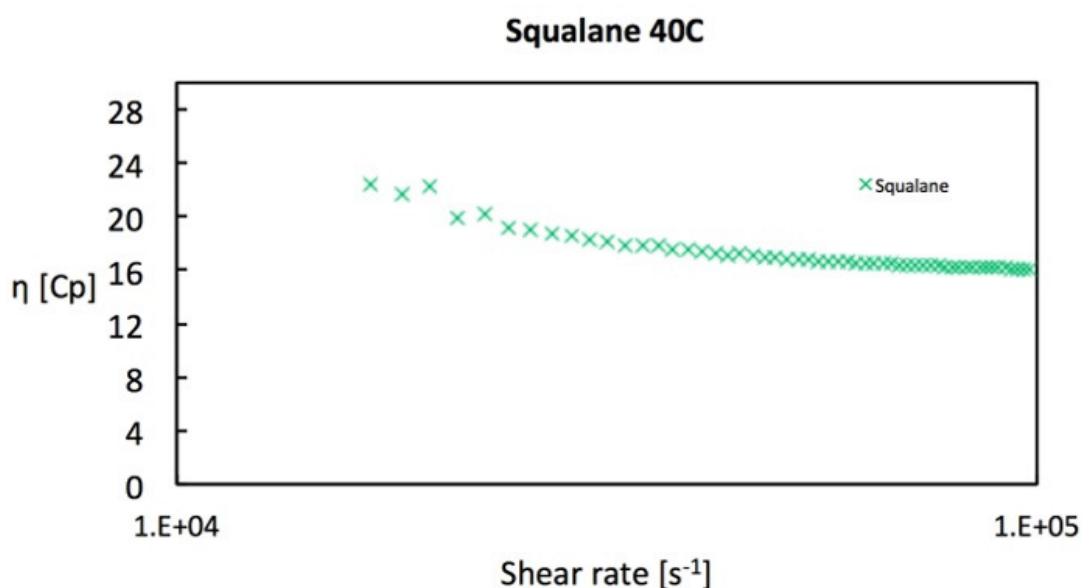


Fig. 10.2: Mid shear measurements on squalane at 40C

10.2.2 MID SHEAR CAPILLARY VISCOMETER

Another, very different type of viscometer was developed in this project to produce flow curves; a capillary viscometer.

A high pressure syringe pump (up to 500 PSI) is connected to a capillary tube as shown in figure 10.3. The pressure drop over the capillary tube is measured by a pressure sensor and flow speed is controlled by the pressure syringe pump. This data, in conjunction with the known dimensions of the tube, allows viscosity and shear rate to be calculated. A heated liquid flow temperature chamber was added at a later stage. Some results were obtained on Newtonian lubricants indicating the usefulness of the rig. However the capillary often got clogged and the liquid temperature chamber created around the syringe was not reliable at keeping the heating liquid sealed.

It is considered that this instrument could produce useful results in the range 3×10^3 - $3 \times 10^5 \text{ s}^{-1}$, but due to time constraints and the effectiveness of the mid-range USV it was not developed further.



Fig. 10.3: Pressure syringe viscometer

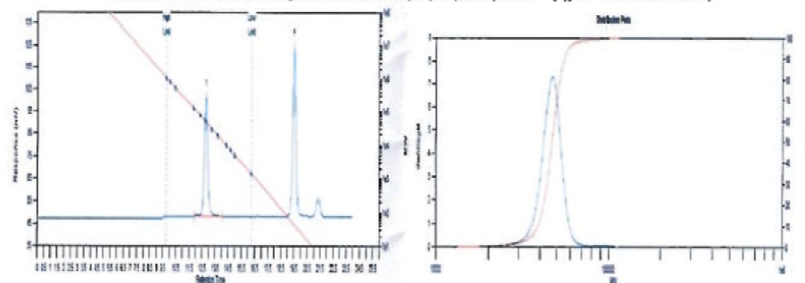
10.3 MODEL POLYMERS, SUPPLIED INFORMATION

CERTIFICATE OF ANALYSIS

Product Polystyrene Mp 47,190
 Batch Number 0006225844
 Part Numbers PL2013-3001, PL2013-3005, PL2013-3010

	GPC	Light scattering	Viscometry
Mp (g/mol)	47,190		
Mn (g/mol)	45,390		
Mw (g/mol)	46,890	49,530	
Mv (g/mol)	46,670		
	Mw/Mn = 1.03		[η] = 0.2472 dl/g

Mp, Mn, Mw & Mv are the respective peak, number, weight and viscosity molecular weight averages
 Mw/Mn = molecular weight distribution or polydispersity ratio [η] = Intrinsic viscosity



Analysis Conditions

	GPC	Light scattering	Viscometry
System	Cirrus GPC / SEC	Agilent 1260 GPC/SEC MDS	Agilent 1260 GPC/SEC MDS
Detector	Ultra violet	1260 Infinity Dual Angle LS	1260 Infinity Viscometer
Columns	2 x PLgel MIXED-C 5 μ m 300 x 7.5mm	PLgel 10 μ m MIXED-BLS 300x7.5mm	PLgel 10 μ m MIXED-BLS 300x7.5mm
Solvent	THF	THF	THF
Flow rate	1.0 ml / min	1.0 ml / min	1.0 ml / min
Injection volume	20 μ l	100 μ l	100 μ l
Sample concentration	0.05%	2.8600 mg / ml	2.8600 mg / ml
Temperature	Ambient	30°C	30°C
Calibrants	Polystyrene	Polystyrene	Polystyrene
Angle		90°	
dn/dc		0.185 g/ml	

The above characterisation data has been measured according to our Quality Control procedures.

Certificate of Analysis valid until expiry date – 18th May 2024

Agilent Manufacturing Site: Essex Road, Church Stretton, Shropshire, SY6 6AX, UK

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Issue 1 23rd May 2014

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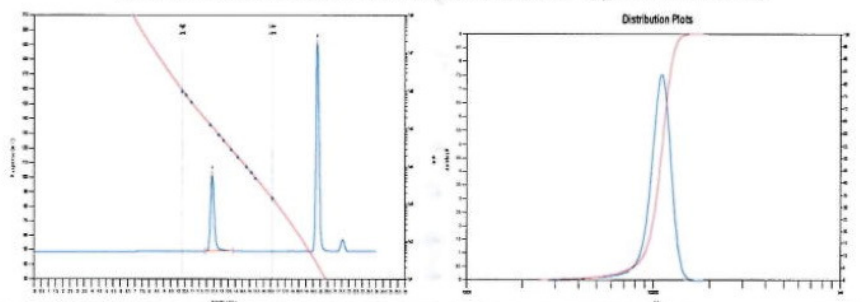
Fig. 10.4: Polystyrene 50k g/Mol

CERTIFICATE OF ANALYSIS

Product Polystyrene **Mp 110,500**
Batch Number 0006304435
Part Numbers PL2013-5001, PL2013-5005, PL2013-5010

	GPC	Light scattering	Viscometry
Mp (g/mol)	110,500		
Mn (g/mol)	103,000		
Mw (g/mol)	106,700	106,500	
Mv (g/mol)	106,200		
	Mw/Mn = 1.03		$[\eta] = 0.4429 \text{ dl/g}$

Mp, Mn, Mw & Mv are the respective peak, number, weight and viscosity molecular weight averages
 Mw/Mn = molecular weight distribution or polydispersity ratio $[\eta]$ = Intrinsic viscosity



Analysis Conditions

	GPC	Light scattering	Viscometry
System	Cirrus GPC / SEC	Agilent 1260 GPC/SEC MDS	Agilent 1260 GPC/SEC MDS
Detector	Ultra violet	1260 Infinity Dual Angle LS	1260 Infinity Viscometer
Columns	2 x PLgel MIXED-C 5 μ m 300x7.5mm	PLgel 10 μ m MIXED-BLS 300x7.5mm	PLgel 10 μ m MIXED-BLS 300x7.5mm
Solvent	THF	THF	THF
Flow rate	1.0 ml / min	1.0 ml / min	1.0 ml / min
Injection volume	20 μ l	100 μ l	100 μ l
Sample concentration	0.05%	2.1132 mg / ml	2.1132 mg / ml
Temperature	Ambient	30°C	30°C
Calibrants	Polystyrene	Polystyrene	Polystyrene
Angle		90°	
dn/dc		0.185 g/ml	

The above characterisation data has been measured according to our Quality Control procedures.

Certificate of Analysis valid until expiry date – 16th December 2025

Agilent Manufacturing Site: Essex Road, Church Stretton, Shropshire, SY6 6AX, UK

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Quality Department

Issue 1 18th December 2015

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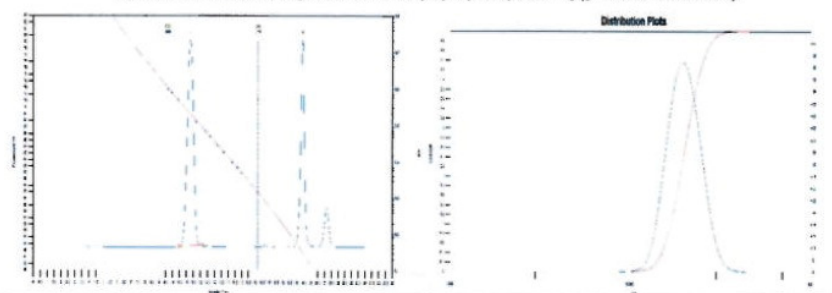
Fig. 10.5: Polystyrene 100k g/Mol

CERTIFICATE OF ANALYSIS

Product Polystyrene **Mp 195,300**
Batch Number 0006266750
Part Numbers PL2013-7001, PL2013-7005, PL2013-7010

	GPC	Light scattering	Viscometry
Mp (g/mol)	195,300		
Mn (g/mol)	195,500		
Mw (g/mol)	203,800	196,600	
Mv (g/mol)	202,600		
	Mw/Mn = 1.04		[η] = 0.6890 dl/g

Mp, Mn, Mw & Mv are the respective peak, number, weight and viscosity molecular weight averages
 Mw/Mn = molecular weight distribution or polydispersity ratio [η] = Intrinsic viscosity



Analysis Conditions

	GPC	Light scattering	Viscometry
System	Cirrus GPC / SEC	Agilent 1260 GPC/SEC MDS	Agilent 1260 GPC/SEC MDS
Detector	Ultra violet	1260 Infinity Dual Angle LS	1260 Infinity Viscometer
Columns	2x PLgel MIXED-C 5μm 300 x 7.5mm	PLgel 10μm MIXED-BLS 300x7.5mm	PLgel 10μm MIXED-BLS 300x7.5mm
Solvent	THF	THF	THF
Flow rate	1.0 ml / min	1.0 ml / min	1.0 ml / min
Injection volume	20μl	100μl	100μl
Sample concentration	0.05%	1.9400 mg / ml	1.9400 mg / ml
Temperature	Ambient	30°C	30°C
Calibrants	Polystyrene	Polystyrene	Polystyrene
Angle		90°	
dn/dc		0.185 g/ml	

The above characterisation data has been measured according to our Quality Control procedures.

Certificate of Analysis valid until expiry date – 18th March 2025

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Issue 1 20th March 2015

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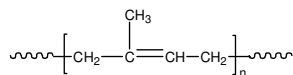


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Fig. 10.6: Polystyrene 200k g/Mol

Sample Name: Polyisoprene, rich in 1,4-addition

Sample #: P18956-1p



Composition:

Mn x 10 ³	Mw/Mn
103.0	1.07

Microstructure:

1,4-addition		1,2- & 3,4-addition
Cis-isomer	Trans-isomer	
87 %	13 %	—

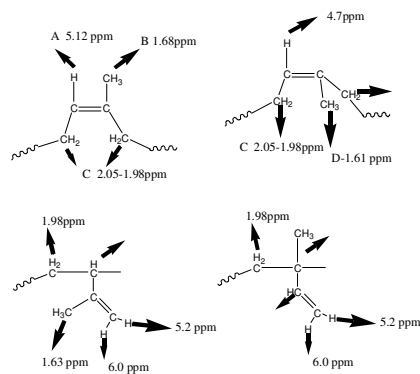
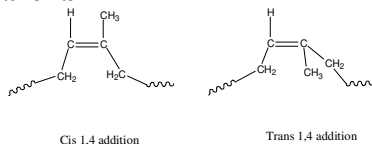
Synthesis Procedure:

Polyisoprene was obtained by living anionic polymerization.

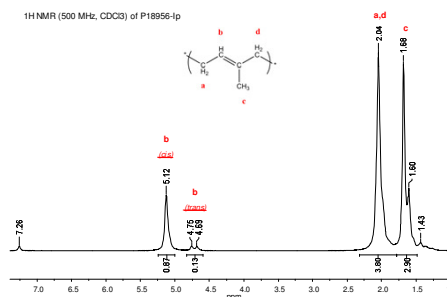
Characterization:

The microstructure of polymer was calculated from ¹H NMR data. Molecular weight and polydispersity index (M_w/M_n) of the polymer were determined by size exclusion chromatography (SEC).

Proton shifts in ¹H NMR:



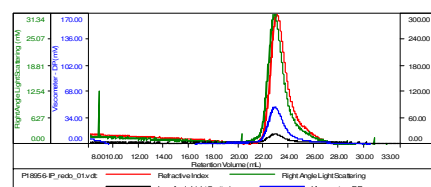
¹H NMR (500 MHz: CDCl₃) of polyisoprene:



SEC elugram of polyisoprene:

Sample ID: P18956-1p

Concentration (mg/mL)	3.456
Sample dilution (mL/g)	0.1200
Method File	FS80KNOV-2014-0003.wcm
Column Set	3x PL 1113 (6000)
Solvent	THF



Sample	MW Number Average (Da)	MW Weight Average (Da)	MW at Peak (Da)	Polydispersity	Intrinsic Viscosity (dL/g)
P18956-1p_retp_01.vcl	103,163	110,596	110,278	1.072	0.5130

(v. I-01)

Fig. 10.7: Polyisoprene 100k g/Mol

