

Effect of polymers on lubricant rheology in an elastohydrodynamic contact

by

Éliane Gendreau

Thesis submitted for the degree of
Doctor of Philosophy

December 2022

Tribology Group
Department of Mechanical Engineering
Imperial College London

Declaration of originality

I declare that the work presented in this thesis is my own, except where otherwise mentioned or referenced.

Declaration of Copyright

The copyright of this thesis rests with the author. Unless otherwise indicated, its contents are licensed under a Creative Commons Attribution - Non Commercial 4.0 International Licence (CC BY-NC).

Under this licence, you may copy and redistribute the material in any medium or format. You may also create and distribute modified versions of the work. This is on the condition that: you credit the author and do not use it, or any derivative works, for a commercial purpose.

When reusing or sharing this work, ensure you make the licence terms clear to others by naming the licence and linking to the licence text. Where a work has been adapted, you should indicate that the work has been changed and describe those changes.

Please seek permission from the copyright holder for uses of this work that are not included in this licence or permitted under UK Copyright Law.

Abstract

Understanding the behaviour of fluids in a tribological contact is crucial to design better lubricants and enhance energy efficiency through friction reduction. Obtaining local and *in situ* insights into tribological contacts is a significant challenge. All the more for complex fluids such as polymer solutions, which are likely to exhibit non-Newtonian and unpredictable behaviours in a tribological contact in the elastohydrodynamic lubrication regime.

In order to gain greater knowledge on the link between the molecular properties of polymers, their mechanisms at the microscale and the rheology of polymer-containing lubricants, new *in situ* techniques were developed. Using phosphorescence imaging velocimetry, Raman spectroscopy, fluorescence anisotropy, and fluorescence lifetime, the behaviour of polymer solutions was investigated in a ball-on-disc contact in the elastohydrodynamic regime, under high-pressure and high-shear.

The flow behaviour of polymer and copolymer solutions deviates from a Couette flow, their velocity profiles exhibit slip and plugs. Quantification of the adsorption supports the hypothesis that the adsorption of polymer molecules on the contact surfaces promotes deviations from a Couette flow.

Raman spectroscopy was designed for the first time *in situ* in an elastohydrodynamic contact to evaluate the presence of polymer molecules in the contact. No change in polymer concentration was observed at the inlet, in the contact, and at the outlet. These results indicate that, for the polymer solutions investigated, an unexpected film thickness is not caused by aggregation or depletion of polymer molecules at the inlet.

Preliminary work using fluorescence anisotropy to generate viscosity maps of a tribological contact was carried out. Investigation up to a viscosity of 5 Pa·s found a very promising performance of the molecular rotor Bodipy, as a viscosity sensor.

Analytical models, based on Barus- and Eyring-like forms of the viscosity, were developed to estimate the viscosity-pressure relationship of fluids, from friction measurements. Compared to high-pressure viscometry data, a good agreement was found up to 1 GPa. This powerful method is of special interest when no viscometer is available.

Acknowledgements

First of all, my biggest thanks go to my supervisor Dr. Janet Wong. Thank you Janet for having reached out to me with this opportunity, had you not I would not have done a PhD and would not have enjoyed these fantastic years in London. I am grateful for your untiring supervision and support. The road was certainly bumpier when the pandemic hit, but it did not stop us from doing exciting research.

I would like to thank Prof. Hugh Spikes for the fruitful discussions and inspiration. Special thanks are due to Dr. Jie Zhang (Jason aka Champion) for his invaluable help in the lab and for always being there when I needed guidance. I would like to thank the people who have provided assistance with my work. Dr. Jonathan Dench, Dr. Stephen Jeffreys and Bastien Bolle passed their knowledge on the optical setups that I used in this work. Amran Mohamed joined forces in the lab, specifically on polymer solutions and adsorption. Prof. Luca di Mare gave great help on the high-pressure viscometry prediction.

I am very grateful to Shell for funding my PhD and making this research possible. I would like to thank Dr. Sarah Matthews, Dr. Caroline Zinser and Dr. Ian Taylor for their supervision and with whom I hope to continue to work with well into the future, as I pursue my journey in tribology!

A massive shout-out goes to all my friends in and out of the tribology group, who have been there for me through the years. I cherish the memories of the countless Friday beers, cakes, lost bets, good laughs, highs and lows! I feel extremely lucky to have shared these happy times with my amazing friends who are too many to list.

Finally, I would like to thank my parents and my brothers for their unconditional love and for always being there for me.

Contents

Declaration of originality	2
Declaration of Copyright	3
Abstract	4
Acknowledgements	5
List of figures	10
List of tables	15
Nomenclature	17
Acronyms	19
1 Introduction	20
1.1 Context and motivation	20
1.2 Aims and objectives	22
1.3 Layout of this thesis	22
2 Literature review	24
2.1 Elastohydrodynamic lubrication	24
2.2 Lubricant rheology in an elastohydrodynamic contact	26
2.2.1 Velocity profiles	26
2.2.2 High-pressure viscometry	27
2.2.3 EHD friction	28
2.3 Lubricant composition	30
2.4 What are viscosity modifiers and how are they characterised?	31
2.4.1 Viscosity index	31
2.4.2 Mechanisms of polymeric viscosity index improvers	32
2.5 Which polymer viscosity modifiers are commonly used?	33

2.5.1	Polyacrylate polymers	34
2.5.2	Olefin copolymers (OCP)	35
2.5.3	Other common viscosity modifiers	35
2.6	Viscosity modifiers as dual additives	35
2.7	Shear dependence of polymer-containing oils	37
2.7.1	Shear stability	37
2.7.2	Shear-thinning mechanisms	37
2.7.3	Shear-thinning models	39
2.8	Rheology of dilute polymer solutions	39
2.8.1	Polymer solutions	39
2.8.2	Effect of architecture on shear response	40
2.9	Film thickness of polymer solutions	42
2.9.1	Conventional models for EHD film thickness	42
2.9.2	Effect of shear-thinning on the film thickness of polymer solutions	43
2.9.3	Effect of slip on the film thickness of polymer solutions	44
2.9.4	Other effects affecting the film thickness of polymer solutions	44
2.10	Bridging the gap of knowledge between macro- and micro-scale phenomena	45
2.11	Summary and objectives	46
3	Materials and methods	48
3.1	Film thickness measurements using interferometry	48
3.2	Friction measurements	49
3.3	Viscosity and shear thinning characterisation	50
3.3.1	Low-shear viscometry	50
3.3.2	High-shear viscometry	51
3.3.3	Mid-shear viscometry	51
3.4	Experimental rheology techniques to probe the properties of fluids in an EHD contact	54
3.4.1	Spectroscopy techniques applied to EHD contacts	54
3.4.2	Luminescence time-resolved spectroscopy	55
3.4.3	Fluorescence anisotropy	56
3.4.4	In situ Raman spectroscopy	57
4	Flow behaviour of polymer solutions in an elastohydrodynamic contact	59
4.1	Introduction	59
4.2	Methodology	61
4.2.1	Phosphorescence spectroscopy	61
4.2.2	Phosphorescence imaging velocimetry	61
4.2.3	Homogeneity of the film thickness in the contact	67

4.2.4	Background correction	69
4.3	Polymer solutions	71
4.3.1	Choice of the solvent	71
4.3.2	Choice of the polymers	72
4.3.3	Preparation of the polymer solutions	74
4.3.4	Characterisation of the size of polymer molecules by dynamic light scattering	74
4.3.5	Flow curves of the polymer solutions	76
4.3.6	Film thickness of the polymer solutions	78
4.3.7	Adsorption of the polymer solutions	80
4.4	Results and discussions	82
4.4.1	Proof of concept - velocity profile of a neat oil, TOTM	82
4.4.2	Velocity profiles of polymer solutions	83
4.4.3	Velocity profiles of copolymer solutions	86
4.5	Conclusions	89
5	In situ investigation of the composition of polymer solutions in a tribological contact in the elastohydrodynamic lubrication regime	90
5.1	Introduction	90
5.2	Film thickness of polymer solutions	91
5.3	Novel experimental setup and methodology	93
5.3.1	Polymer solutions and experimental conditions	93
5.3.2	Home-built <i>in situ</i> Raman spectroscopy setup	95
5.3.3	Validation of the Raman spectra	97
5.3.4	Size of polymer molecules in polymer solutions	99
5.3.5	Shear-thinning behaviour	100
5.3.6	Experimental measurements of the film thickness of polymer solutions	101
5.3.7	Performing chemical analysis in a tribological contact	104
5.3.8	Deconvolution of two overlapping peaks	108
5.3.9	Limitation on film thickness	109
5.4	Results	110
5.4.1	Effect of concentration	110
5.4.2	Do polymer molecules enter the tribological contact?	112
5.4.3	Effect of slide-roll ratio	113
5.5	Conclusions	114
6	Local viscosity measurements in a tribological contact in the elastohydrodynamic regime	116
6.1	Measuring local viscosity <i>in situ</i> in an EHD contact	116

6.2	Fluorescence anisotropy using a LED for <i>in situ</i> viscosity measurements .	117
6.2.1	Materials and methods	117
6.2.2	Anisotropy-viscosity calibration in bulk	119
6.2.3	Ball-on-disc EHD contact imaging	120
6.2.4	Recommendations for future work	122
6.3	Fluorescence lifetime spectroscopy for viscosity mapping of EHD contacts	123
6.3.1	Bodipy as a novel fluorophore for viscosity mapping in EHD contacts	123
6.3.2	Materials and methods	124
6.3.3	Lifetime-viscosity calibration in bulk	126
6.3.4	In situ viscosity maps using fluorescence lifetime spectroscopy . .	127
6.4	Conclusions	128
7	Bridging the gap between friction and viscometry at high pressure: estimation of the viscosity-pressure behaviour of a fluid from friction measurements	129
7.1	Introduction	129
7.2	Methodology	130
7.2.1	Low shear viscosity	131
7.2.2	EHD friction	132
7.2.3	EHD film thickness	134
7.3	Thermal effects in the contact and correction	135
7.3.1	Temperature rise in the contact	136
7.3.2	Isothermal shear stress	137
7.3.3	Average viscosity	139
7.4	Linking friction measurements to lubricant rheology	139
7.5	Non-linear least square procedure	140
7.6	Functional forms for the viscosity	141
7.7	Sensitivity analysis	142
7.8	Results	145
7.9	Conclusions	148
8	Conclusions and future work	149
8.1	Summary of findings	150
8.2	Limitations	152
8.3	Recommendations for future work	153
	References	154

List of Figures

2.1	Stribeck curve and the lubrication regimes	25
2.2	Contact pressures found in some engineering systems, adapted from Zhang and Spikes [15]	26
2.3	Some possible velocity profiles in a contact in the elastohydrodynamic regime, adapted from [27]	27
2.4	Pressure distribution of a point EHD point contact. (a) Hertzian pressure distribution prediction. (b) Pressure distribution from the numerical solution of the EHD problem.	29
2.5	Examples of frictional responses, limiting shear stress and isothermally corrected shear stress.	30
2.6	PMA	34
2.7	PAMA	34
2.8	OCP	35
2.9	Film forming properties of viscosity modifier solutions in the boundary regime. Taken from [80], originally from [78].	36
2.10	Friction performance of a block copolymer (PFM B) in different base oils, at 30 °C, adapted from [82].	36
2.11	Flow curve of a polymer solution (Group II base oil + 13.5 wt% OCP), adapted from [94].	38
2.12	Types of polymer architecture (a) linear, (b) ring, (c) star, (d) H, (e) comb, (f) ladder, (g) dendrimer, (h) randomly branched, adapted from [98]. . .	40
2.13	Central film thickness of PAO-650, comparison between calculation from Hamrock & Dowson (equation 2.9a) and experimental data, adapted from [111].	43
3.1	Central film thickness of DEHS at different temperatures, with pure rolling conditions and the steel ball loaded (20 N) against the glass disc.	49
3.2	Viscosity of dibutyl phthalate	50

3.3	Flow curve for squalane, at 60 °C. Black dotted line represents low shear viscosity value. Insert shows all data points at low shear rate (Stabinger viscometer), medium (big gap configuration) and high shear rates (USV standard configuration).	51
3.4	Viscosity of (a) squalane and (b,c) two polymer solutions measured using the big gap configuration of the USV	52
3.5	Standard deviation calculated over 30 repeats for 14 fluids tested at 4 shear rates	53
3.6	Absorption (dashed) and fluorescence emission (filled) spectra of Nile red. Excitation wavelength is 488 nm (blue). Generated using [142].	55
3.7	Fluorescence anisotropy: the incident light is polarised, the light emitted by the dye molecules is depolarised.	57
3.8	Raman spectrum of PAO 150	58
4.1	Schematic of the phosphorescence spectroscopy setup, with a zoomed-in representation of the ball-on-disc contact in the elastohydrodynamic regime on the left-hand side, in which the blue lines represent the initial column of excited dye molecules after the laser pulse at t_0 and how they would spread after a short time Δt in the case of a Couette flow. An example of phosphorescence images is shown above the contact.	62
4.2	Chemical structure of Eu(DBM)3(Phen) and its phosphorescence lifetime in DOP and DOP + copolymer	63
4.3	Intensity distributions of the phosphorescence response after laser excitation.	64
4.4	Phosphorescence images, normalised intensities and velocity profiles. The first image is taken as the time reference. The dashed line in the velocity profile corresponds to a Couette flow.	66
4.5	SLIM images and film thickness for DBP + 8 wt% PS 35 kDa, at $T=25$ °C and $P_{max} = 526$ MPa, steel ball against glass disc contact.	68
4.6	Intensity over time for DOP, $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C. First image is taken as time reference. Flow direction is left to right on each set of pictures	69
4.7	Background phosphorescence images for DOP, $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C. First image is taken as time reference. Flow direction is left to right.	70
4.8	Chemical structure of esters used	71
4.9	Chemical structure of polymers used	73
4.10	Distributions of the size of PS molecules in DBP and DOP at different concentrations at 25 °C. Inserts show the size of maximum intensity in the distribution against PS concentration.	75

4.11	Distributions of the size of the copolymer molecules in DBP at 25 °C. Measurements performed by Amran Mohamed	76
4.12	Viscosity at 60 °C as a function of shear rate for (a) DOP and DBP, (b) PS ($M_n = 35 \text{ kDa}$) in DBP, (c) PS ($M_n = 35 \text{ kDa}$) in DOP, (d) PS ($M_n = 192 \text{ kDa}$) in DBP, (e) PS ($M_n = 192 \text{ kDa}$) in DOP. Different symbols are used for the data points from the low-shear Stabinger viscometer (circles), the mid-shear USV (crosses) and high-shear USV (triangles).	77
4.13	Film thickness of DBP + 9.9 wt% PS 192 kDa and DOP + 4.8 wt% PS 192 kDa, at SRR = 0 % (blue) and -180 % (red), T=21 °C and $P_{max} = 418 \text{ MPa}$, steel ball against glass disc contact.	78
4.14	Film thickness of DOP + 4.8 wt% PS 192 kDa, at SRR = 0 %, T=21 °C and $P_{max} = 418 \text{ MPa}$, steel ball against glass disc contact. Dotted lines are predictions using Chittenden (equation 7.8).	79
4.15	Film thickness of DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa (short) and DOP + 0.05 wt% PS-b-PAA 197.0-b-190 kDa (long), at room temperature and $P_{max} = 418 \text{ MPa}$, steel ball against glass disc contact.	80
4.16	Mass adsorbed on QCM crystal over time. Toluene is the baseline. Test fluids are DBP and DBP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa. From Amran Mohamed.	81
4.17	Phosphorescence images and velocity profiles for TOTM, $U_e=0.3 \text{ m/s}$, T=30 °C, SRR = 50 % (disc faster), glass ball against glass disc.	83
4.18	Background corrected and normalised phosphorescence images, and velocity profiles. The first image is taken as the time reference. Grey lines and orange lines represent the position of the disc and the ball, respectively. Dashed lines in velocity profiles correspond to a Couette flow. All three tests are done in pure sliding, with $P_{max}=188 \text{ MPa}$, $U_e=0.3 \text{ m/s}$ and T=25 °C.	85
4.19	DOP, DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa and DOP + 0.05 wt% PS-b-PAA 197-b-190 kDa, in pure sliding (ball rotates), with $P_{max}=188 \text{ MPa}$, $U_e=0.3 \text{ m/s}$ and T=25 °C. (a), (b) and (c) are background corrected phosphorescence images, direction of the flow is left to right, (d) are the corresponding reconstructed velocity profiles.	87
4.20	DOP + 0.5 wt% PS-b-PAA 41k-b-4.2k, in pure sliding, with $P_{max}=188 \text{ MPa}$, $U_e=0.3 \text{ m/s}$ and T=25 °C.	88
4.21	Comparison of flow profiles at SRR of +180 % (disc faster) and -200 % (ball faster), DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa, with $P_{max}=188 \text{ MPa}$, $U_e=0.3 \text{ m/s}$ and T=25 °C.	89
5.1	Film thickness of polymer solutions	92

5.2	Chemistry of a typical PAO and polybutene	94
5.3	Schematic of Raman spectroscopy	95
5.4	Schematic of the ball-on-disc contact with image of the contact. The red dashed circle highlights the contact, the red cross highlights the centre of the contact.	96
5.5	Laser spot in a loaded contact under static conditions.	96
5.6	Comparison between Raman spectra acquired with a WITec Raman imaging microscope (in blue) and the home-built Raman setup (Andor, in red), after baseline correction and normalisation	98
5.7	Raman spectra of PAO 150. The reference is acquired under static conditions (droplet on a glass slide). Comparison between the inlet ($-400\text{ }\mu\text{m}$), the contact and the outlet ($+400\text{ }\mu\text{m}$), in pure rolling, $T = 15\text{ }^{\circ}\text{C}$, $U_e = 0.3\text{ m/s}$, $P_{mean} = 424\text{ MPa}$	99
5.8	Size of polymer molecules measured by dynamic light scattering	99
5.9	Viscosity as a function of shear rate for PAO 50, PAO 150, and the polymer solutions, at $100\text{ }^{\circ}\text{C}$. Different symbols are used for the data points from the low-shear Stabinger viscometer (stars), the mid-shear USV (circles) and high-shear USV (triangles). The horizontal lines represent the low-shear viscosity values. Green data points (PAO 150 + 10 wt% PB 1300) are overlapped by PAO 150 in red.	100
5.10	Film thickness of polymer solutions and neat PAO 150 and PAO 50, pure rolling (ball driven), $40\text{ }^{\circ}\text{C}$	101
5.11	Film thickness at 4 different entrainment speeds, against viscosity ($T=40\text{ }^{\circ}\text{C}$)	102
5.12	Effect of temperature on film thickness	103
5.13	Effect of load and material on film thickness: experimental measures and correction using Chittenden and Dowson.	103
5.14	Raman spectra of neat polybutene and neat PAO 50 under static conditions. The peaks are identified with the vertical lines of corresponding colours. Red arrows highlight the peaks selected for the analysis.	104
5.15	Raman spectra of the neat fluids, Andor spectrometer	105
5.16	Raman spectra for neat polybutene, neat PAO 50 and a blend of PAO 50 + 50 wt% polybutene . The three spectra at the bottom are acquired under static conditions. The spectrum at the top for PAO 50 + 50 wt% polybutene is acquired in the contact, under pure rolling conditions, at $T = 26\text{ }^{\circ}\text{C}$, $U_e = 1\text{ m/s}$, $P_{mean} = 424\text{ MPa}$. A peak corresponding to the polymer molecules is clearly visible in the contact (red circle).	106
5.17	Raman spectrum before baseline correction in blue. The baseline is in red, and the fitted final Raman spectrum used for further analysis in yellow. .	107

5.18	Raman spectrum of PAO 150 + 30 wt% PB (M_n 2300 Da) in pure rolling, $T = 25\text{ }^\circ\text{C}$, $U_e = 0.3\text{ m/s}$, $P_{mean} = 424\text{ MPa}$. The three sapphire peaks are identified with the vertical lines.	107
5.19	(a) and (c): Raman spectra highlighting a polymer peak and a sapphire peak close to each other. The red vertical line represents the polymer peak (729 cm^{-1}), and the blue vertical line the sapphire peak (760 cm^{-1}). (b) and (d): Respective deconvolution with a Gaussian fit of the two peaks. .	108
5.20	Raman spectra of PAO 150 + 30 wt% PB ($M_n = 2300\text{ Da}$) at different temperatures, at the centre of the contact, $U_e = 0.3\text{ m/s}$, $P_{mean} = 424\text{ MPa}$, $SRR = 0\text{ }\%$	109
5.21	The four ratio of intensities $I_{PB\text{ peak}}/I_{PAO\text{ peak}}$ against temperature, for the six polymer solutions under static conditions.	110
5.22	Ratio of intensities between polymer peaks and PAO peaks in the Raman spectrum against polymer concentration. Markers are experimental data points, lines are polynomial fits (order 2).	111
5.23	Normalised intensity at different positions from the inlet to the outlet, PAO 150 + 30 wt% polybutene ($M_n = 2300\text{ Da}$), pure sliding ($SRR = -200\%$), entrainment speed 0.3 m/s, 15 $^\circ\text{C}$. Insert is a zoom-in for greater clarity.	112
5.24	PAO 150 + 30 wt% polybutene ($M_n = 2300\text{ Da}$), pure sliding ($SRR = -200\%$), entrainment speed 0.3 m/s, 15 $^\circ\text{C}$. The vertical dashed lines represent the diameter of the contact.	113
5.25	PAO 150 + 30 wt% PB ($M_n = 2300\text{ Da}$), $T = 15\text{ }^\circ\text{C}$ $U_e = 0.3\text{ m/s}$, $P_{mean} = 424\text{ MPa}$. $SRR = -200\text{ }\%$ is pure sliding with a stationary disc, $SRR = +200\text{ }\%$ is pure sliding with a stationary ball.	114
6.1	Fluorescence anisotropy optical setup	118
6.2	Calibration anisotropy-viscosity, error bars are standard deviations, dotted line is best fit. Dye is Nile Red. Polymer solutions are highlighted in red (PAO 8) and pink (PAO 4). Insert is linear plot.	120
6.3	Intensity for VH and VV configurations of the polarisers, and corresponding anisotropy distribution. PAO 8 + Nile Red, pure rolling, $U_e = 150\text{ mm/s}$, $P_{max} = 287\text{ MPa}$. Flow direction is bottom to top. Note that in order to visualise the contact clearly, the intensity scales are different in figures (a) and (b). In (c), black circle represents the ball-on-disc contact.	121
6.4	Fluorescence lifetime of Bodipy C10 as a function of viscosity measured at different temperatures. The solutions used are mixtures of methanol-glycerol of different viscosities. Adapted from [178].	123
6.5	Bodipy C10	124
6.6	Fluorescence lifetime spectroscopy setup	125

6.7	Normalised photocount over time for PAO 8 + Bodipy C10 under static conditions. The lifetime τ is given for each of the three decay curves, from a mono-exponential fit. Blue line is the photocount, red, yellow and purple lines are fits.	125
6.8	Calibration lifetime-viscosity, dotted line is best fit. Dye is Bodipy C10. Polymer solution is highlighted in red. Insert is linear plot.	126
6.9	Variation of (a) lifetime and corresponding (b) viscosity for PAO 8 doped with Bodipy C10. $P_{max} = 303 \text{ MPa}$, $U_e = 150 \text{ mm/s}$, pure rolling. Theoretical contact radius is $a = 77 \text{ }\mu\text{m}$	127
7.1	Flow chart for viscosity prediction from friction and film thickness tests .	131
7.2	Schematic of a ball-on-disc contact of radius a and central film thickness h_c . In the elastohydrodynamic regime, the two surfaces are fully separated by the lubricant film (not to scale).	132
7.3	Central film thickness for PAO 8, measured, fitted using equation (7.7) and estimated using [172].	135
7.4	Average shear stress against strain rate for DEHS at four mean contact pressures, accessed using different pairs of contact materials. The supply temperature is $30 \text{ }^\circ\text{C}$. The solid lines represent the estimated isothermal average shear stress, capped at a maximum temperature rise in the contact of $10 \text{ }^\circ\text{C}$	138
7.5	Isothermal average shear stress against strain rate for DEHS at five mean contact pressures. The solid lines are the corresponding linear regression of the linear regions, which slopes are the average viscosities $\bar{\eta}$	139
7.6	Viscosity-pressure behaviour for DEHS and PAO 8. The solid lines are the viscosity estimated from friction using the two functional forms, the black symbols are the high-pressure rheometry data provided by Bair (private communication). Insert highlights the region 0-0.8 GPa in linear-linear axes.	146
7.7	Comparison between measured and estimated shear stress. τ_{MTM} is the isothermally corrected shear stress from friction experiments, τ_{fit} is the shear stress calculated using the viscosity estimated with the Eyring-like form.	147

List of Tables

2.1	Thickening mechanisms of viscosity modifiers	33
3.1	Material properties of specimens used in film thickness measurements with the EHD2	49
3.2	Mean standard deviation over 14 tests for the four shear rates in the big gap configuration of the USV	53
3.3	Spectroscopy techniques developed for <i>in situ</i> observations of an EHD contact	54
4.1	Viscosity and film thickness of the esters	72
4.2	Polymers considered for this study	73
4.3	Copolymers PS-b-PAA and their properties	74
4.4	Polymer solutions characteristics	84
4.5	Copolymer solutions characteristics	86
5.1	Solvents and polymer solutions, dynamic viscosity and film thickness . .	94
5.2	Experimental conditions for the Raman spectroscopy technique	94
5.3	Material properties of specimens used in the Raman spectroscopy experiments	94
5.4	Raman spectroscopy: polybutene, PAO and sapphire peaks (in cm^{-1}). Peaks selected for the analysis are in red.	104
5.5	Comparison of the intensities at the peaks before and after deconvolution	109
6.1	Fluids used for fluorescence anisotropy and viscosity	119
6.2	Fluids used for fluorescence lifetime spectroscopy and viscosity	126
7.1	Viscosity of tested fluids	131
7.2	Properties of the materials used in the friction tests	132
7.3	Reduced moduli and pressure ranges for the tested pairs of specimens . .	133
7.4	Estimated thermal conductivity K_{oil} (W/mK)	136
7.5	Uncertainties and their determination method.	143
7.6	Contribution of experimental uncertainties on the sensitivity of the fit. .	144
7.7	Best fit for the viscosity derived from friction for DEHS and PAO 8 . . .	145

Nomenclature

A	contact area (m ²)	q_v	rate of heat generation per unit volume (W/m ³)
a	contact radius (m)	R	equivalent radius of the Hertzian contact (m)
c	specific heat capacity (J/kg·K)	r	distance from contact centre (m)
E	elastic modulus (Pa)	R_x	reduced radius of curvature in the entrainment direction (m)
E^*	reduced elastic modulus (Pa)	SRR	slide-roll ratio
F	frictional force (N)	ΔT	temperature rise (K)
$\bar{G}$	dimensionless material parameter	T	temperature (K)
h	film thickness (m)	t	time (s)
h_c	central film thickness (m)	$\bar{U}$	dimensionless speed parameter
I	Intensity	ΔU	sliding speed (m/s)
K	thermal conductivity (W/m·K)	$u(z)$	through film velocity (m/s)
M_n	number average molecular weight (Da)	u_1	surface velocity of surface 1 (m/s)
M_w	weight average molecular weight (Da)	u_2	surface velocity of surface 2 (m/s)
$\bar{P}$	mean Hertzian pressure (Pa)	U_e	entrainment speed (m/s)
P	pressure (Pa)	VI	viscosity index
P_{max}	maximum Hertzian pressure (Pa)	$\bar{W}$	dimensionless load parameter
$PSSI$	permanent shear stability index	W	normal load (N)
		Greek letters	
		α	viscosity-pressure coefficient (Pa ⁻¹)

α^*	reciprocal asymptotic isoviscous pressure (Pa ⁻¹)
$\bar{\eta}$	average dynamic viscosity of the contact (Pa·s)
η	dynamic viscosity at pressure P (Pa·s)
η_0	dynamic viscosity at atmospheric pressure (Pa·s)
$\dot{\gamma}$	shear rate (s ⁻¹)
μ	coefficient of friction
ν	Poisson's ratio
ρ	density (kg/m ³)
$\bar{\tau}$	average shear stress in the contact (Pa)
τ	shear stress (Pa)
τ_e	Eyring shear stress (Pa)

Fluorescence

$I_{\parallel}$	vertically polarised intensity
$I_{\perp}$	horizontally polarised intensity
r	anisotropy
τ	lifetime (s)

Least square procedure

α	vector of the parameters to be fitted
$\mathcal{E}$	error
$\mathbf{g}^{(\cdot)}$	transfer matrix
$\mathbf{g}$	gradient vector of E
$\mathbf{H}$	Hessian matrix of E
r	residuals between experimental and fitted values
$\ \cdot\ $	Frobenius norm

Acronyms

APD	Avalanche Photodiode	PMA	Poly(methyl acrylate)
BBO	Barium Borate Oxide	PMMA	Poly(methyl methacrylate)
CCD	Charge Coupled Device	PS	Polystyrene
DBP	Dibutyl Phthalate	PSSI	Permanent Shear Stability Index
DEHS	Bis(2-ethylhexyl) sebacate	PVL	Permanent Viscosity Loss
DEP	Diethyl Phthalate	QCM	Quartz Crystal Microbalance
DLS	Dynamic Light Scattering	SBR	Styrene Butadiene
DNA	Deoxyribonucleic Acid	SIP	Styrene Isoprene Polymer
DOP	Dioctyl Phthalate	SLIM	Spacer Layer Imaging Method
EHD	Elastohydrodynamic	SRR	Slide Roll Ratio
EHL	Elastohydrodynamic Lubrication	TCSPC	Time Correlated Single Photon Counting
EMCCD	Electron Multiplying Charge Coupled Device	TOTM	Trioctyl Trimellitate
ETM	Extreme pressure Traction Machine	USV	Ultra Shear Viscometer
FWHM	Full Width Half Minimum	VI	Viscosity Index
LED	Light Emitting Diode	VM	Viscosity Modifier
MTM	Mini Traction Machine	5P4E	5-phenyl-4-ether
NA	Numerical Aperture		
OCP	Olefin Copolymers		
PAA	Polyacrylic Acid		
PAMA	Polyalkylmethacrylate		
PAO	Polyalphaolefin		
PB	Polybutene		
PFM	Polymeric Friction Modifiers		
PIB	Polyisobutylene		
PISH	Poly(isoprene-styrene hydrogenated)		

Chapter 1

Introduction

This project, titled *Effect of polymers on lubricant rheology in an elastohydrodynamic contact*, is introduced in this chapter. The background underlying this research is explained, and the aims and objectives are presented. Finally, the structure of this PhD thesis is given.

1.1 Context and motivation

The growing awareness of the importance of CO₂ emission reduction contributes to the improvement of the energy efficiency of vehicles. In 2020, despite a fall of 19 % between 2019 and 2020 attributed to the COVID-19 pandemic, transport accounted for 24 % greenhouse gas emissions in the UK [1], of which 52 % came from passenger cars [2]. Car manufacturers are compelled to enhance fuel efficiency while facing increasingly stringent emission regulations. For example, the average passenger car CO₂ emissions target for 2021 in the European Union was 95 gCO₂/km which corresponded to a decrease of more than 20 % in comparison with the 2015 target [3]. The new targets for car manufacturers are to reduce the average CO₂ of their new passenger car fleet by 15 % for the period 2025-2029 and by 37.5 % from 2030 onwards [4]. One-third of fuel consumption in passenger cars is spent overcoming frictional losses, of which 17 % are engine and transmission friction losses, 11 % are tire rolling friction and 5 % are braking friction losses. The remainder of the fuel energy is used in exhaust (33 %), cooling (29 %), and lost in air resistance (5 %) [5]. Consequently, fuel efficiency can be improved through more aerodynamic vehicle designs, new technologies for engines and vehicles, and friction reduction using more effective lubricants.

Lubricants are base oils enhanced with additives, as a base oil by itself cannot provide an effective lubrication in all parts of an engine. Piston rings, journal bearings and valve train apply different temperature and shear rate conditions on the lubricant. Temperatures range from low temperature (depending on the localisation) to 250 °C

in the pistons, and shear rates are up to 10^8 s^{-1} [6]. Hence, additives are needed to make the oil effective under such broad and severe conditions. A fully formulated engine oil can have a weight percentage of additives as high as 15-20 % [7]. These additives include viscosity modifiers, anti-wear additives, friction modifiers, detergents, dispersants, anti-foam additives. Viscosity modifiers typically have a concentration of 5 to 15 wt% depending on their solubility in the base oil and their viscosity [8].

The current trend to reduce friction and thus energy loss is to use lubricants of lower viscosity. Note that viscosity decreases with increasing temperature. This means that if a low viscosity lubricant is used, its viscosity may become too low to maintain a lubricant film that fully separates the lubricated surfaces, resulting in surface contact and hence wear. Therefore, the challenge is to keep an appropriately high viscosity at high temperature to ensure an efficient lubrication, while having the lowest possible viscosity at low temperature.

Viscosity modifiers (VMs) are added to oils to improve the viscosity-temperature dependence of the oil. The first viscosity modifiers used in the 1930s were rubbers, and have developed to large polymer molecules to date. The latest advances include the use of new functional groups and the development of various architectures for these polymer molecules. Star, comb and hyperbranched molecules have proved to be effective viscosity modifiers and have interesting rheological responses compared to their linear counterparts [9, 10]. However, the behaviour of polymer-containing oils under high shear rate and high pressure, and the potential viscoelastic effects, are still not fully understood and poorly predictable. Designing viscosity modifiers that have the most appropriate architecture is difficult. It is a multi-factor problem including VM performance, cost, compatibility with other additives, and flexibility of chemical formulation.

The elastohydrodynamic (EHD) lubrication regime occurs in many engineering systems and engine components such as bearings, gears and cams. In this regime, the fluid experiences extreme conditions of pressure, shear and temperature. However, there is little understanding of the behaviour of the lubricants in this regime. Non-conformal contacts have a diameter of around $100 \mu\text{m}$, the contact surfaces are separated by a thin film of lubricant with a film thickness of less than $1 \mu\text{m}$. The response of the lubricant in such a contact is typically non-Newtonian. The use of viscosity modifier-containing solutions increases the complexity in an EHD contact. More information is needed on the link between the molecular structures and properties of VMs, their molecular behaviour in the contact, and the macro-rheology of the fluid.

Accurate viscosity measurements are crucial for the understanding of lubricant rheology and for the design of efficient oils and engines. Techniques and models are developed to obtain rheological insights but few suitable options are available when it comes to conditions of high pressures and high shear rates. Reproducing the extreme

engine operating conditions in a laboratory is challenging. PCS commercialises the Ultra Shear Viscometer (USV) that can achieve shear rates as high as 10^7 s^{-1} [11]. Bair [12] built a high-pressure viscometer that can apply pressures up to 1.2 GPa. Lubricants can be subjected to both high pressures and high shear rates in friction tests performed using apparatus with a ball-on-flat geometry [13, 14], but when the viscosity is derived from friction, only an average value over the whole contact is obtained, while the viscosity is heterogeneous in a ball-on-flat contact due to the distribution of pressure. These techniques fail to give a complete picture of the lubricant rheology in a contact.

1.2 Aims and objectives

The aim of this study is to understand the rheology of complex fluids in the EHD lubrication regime, across scales. This study focuses on the impact of viscosity modifiers on the local properties of the fluid in the EHD contact, and the effects on the global rheological response of the oil.

The objective of this work is to develop novel *in situ* techniques to allow *in operando* investigation of the local properties of lubricants in an EHD contact. The developed techniques will be applied to viscosity modifier-containing solutions, to access their velocity profiles, to conduct chemical analyses in the contact, and to map the viscosity within the contact. In addition, I seek to develop a methodology capable of predicting the viscosity-pressure response of a fluid from its frictional response.

1.3 Layout of this thesis

This thesis begins in chapter 2 with an overview of the literature covering the rheology of fluids in the EHD lubrication regime. A strong focus of this chapter is on viscosity modifiers, including examples of the commonly used viscosity modifiers, as well as their effects on the rheology and flow of lubricants in the EHD regime. Finally, experimental techniques are critically reviewed.

In chapter 3, the methodology for conventional testing of fluids is described. This chapter provides details on film thickness, friction and viscosity measurements.

In chapter 4, the development of a novel EHD velocimetry technique is presented. The validity of the technique is first assessed with simple fluids and systems of known velocity profiles. Then the flow of polymer and block copolymer solutions is investigated.

In chapter 5, a novel *in situ* technique using Raman spectroscopy to obtain chemical

information of a lubricant in a contact is outlined. First, the rheological response of the polymer solutions (film thickness and shear thinning) is investigated. The chemical analyses of polymer solutions performed *in situ* in an EHD contact are then presented.

Chapter 6 presents two *in situ* techniques to map the viscosity in an EHD contact. Calibration and preliminary results are given for fluorescence anisotropy. A time-resolved fluorescence spectroscopy technique is described, with the proof of concept study conducted using a new fluorescent dye. Lifetime-viscosity calibration and initial results of viscosity maps are given.

In chapter 7, the high-pressure viscometry of fluids is investigated. Models are proposed to predict the viscosity of a fluid from its film thickness and friction measurements. Viscosity-pressure predictions for two base oils are presented and compared with experimental results.

Chapter 8 summarises the main findings of this thesis and provides directions for potential future studies.

Chapter 2

Literature review

This chapter examines the literature on the elastohydrodynamic lubrication regime, first with a focus on the background of elastohydrodynamic lubrication, velocity profiles, and the friction and high-pressure response of lubricants. Then, viscosity modifier additives are overviewed, followed by the shear response and film thickness of polymer solutions.

2.1 Elastohydrodynamic lubrication

Lubricants are an effective way of reducing friction and wear between two rubbing surfaces. Lubricants can be liquid, gaseous or solid. Under the right conditions, they separate the surfaces in contact. For liquid lubricants, the relative movement of the rubbing surfaces entrains the fluid and creates a thin film between them. Several regimes of lubrication can be differentiated and are shown on the Stribeck curve in figure 2.1. The friction coefficient is a function of the dynamic viscosity η , the entrainment speed U_e , and the applied load P . These parameters affect the film thickness and thus the friction. When the film is very thin (low viscosity, low speed and high pressure), the surfaces are in contact, the coefficient of friction is high. The friction is minimum when the film thickness is the thinnest required to fully separate the two surfaces. In full film lubrication, when the speed and viscosity increase, and the pressure decreases, the film becomes thicker in the contact, leading to more friction.

The regimes identified on the Stribeck curve are the following:

- The hydrodynamic lubrication regime is characterised by a full separation of the contact surfaces, and happens at high entrainment speed and low pressure. The coefficient of friction is relatively low in this regime and the lubricant viscosity is the main driver of its value. The coefficient of friction increases with film thickness (higher viscosity, higher speed or lower pressure) due to more internal fluid friction.
- The elastohydrodynamic lubrication (EHL) regime, which occurs for non-conformal

contacts under high pressures, belongs to the full-film lubrication regime, in the region where the coefficient of friction is the smallest. The high pressure causes the contact surfaces to elastically deform. The surfaces are separated by a very thin film of lubricant. The EHL regime is characterised by a Hertzian distribution of pressure in the contact and by a film thickness that is almost uniform in the centre, with a constriction at the outlet and on the sides of the contact.

- When asperities of the surfaces are in contact but the load is also supported by the film of lubricant, the lubrication is called mixed.
- The boundary lubrication regime is the most severe regime, characterised by a high coefficient of friction. The film is too thin to support the load, the latter is hence only supported by the asperities in contact. The conditions promoting this regime are a low entrainment speed, a high pressure and a high temperature (low viscosity).

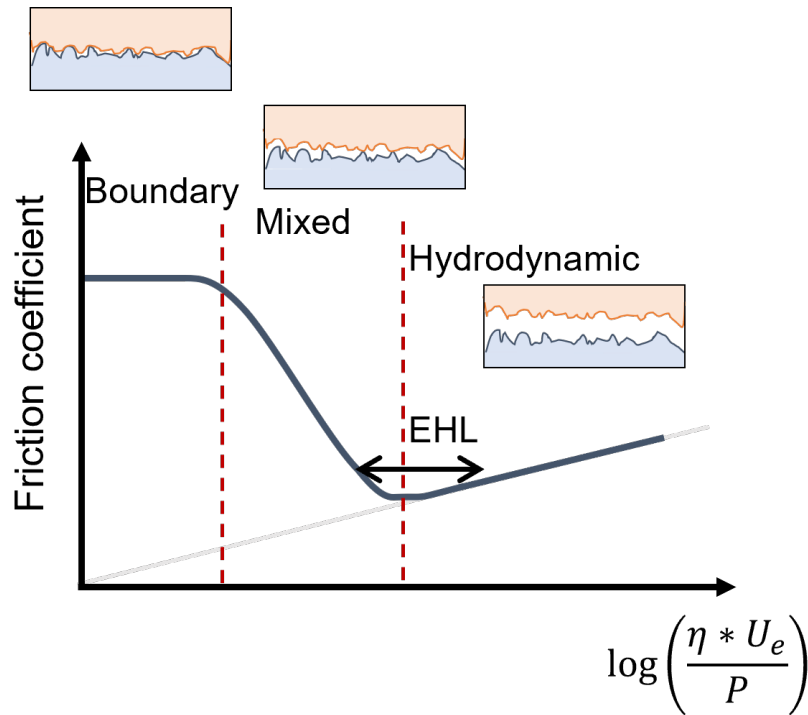


Figure 2.1: Stribeck curve and the lubrication regimes

In the elastohydrodynamic (EHD) regime, the viscosity of the lubricant is impacted by the pressure and can increase by several orders of magnitude in the contact. The pressure is typically around 1-2 GPa but can reach higher values, for example in rolling bearings or other components [15] that are listed in figure 2.2.

Gears	Cams	Rolling bearings	CV joints (ball)	CVTs (toroidal)
1 to 1.8 GPa	1.2 to 1.8 GPa	1 to 3.5 GPa	2 to 4 GPa	2 to 4 GPa
				

Figure 2.2: Contact pressures found in some engineering systems, adapted from Zhang and Spikes [15]

2.2 Lubricant rheology in an elastohydrodynamic contact

2.2.1 Velocity profiles

The Reynolds equation describes the pressure field in the fluid contained between two contact surfaces in relative motion. Assuming (1) a constant pressure through the film, (2) a Newtonian lubricant of uniform viscosity and density through the film, (3) a laminar flow, and (4) given a no-slip boundary condition, the velocity profile $u(z)$ through the thickness of the film is derived as

$$u(z) = \frac{1}{2\eta} \frac{\partial p}{\partial x} (z^2 - zh) + \Delta U \frac{z}{h} \quad (2.1)$$

where u is the velocity of the fluid in the x -direction (direction of the flow), η is the fluid viscosity at pressure p , ΔU is the relative sliding speed, z in the direction perpendicular to the flow and h is the thickness of the fluid. The pressure-driven Poiseuille parabolic velocity is usually negligible due to the piezoviscous effect at the central region of the contact (large lubricant viscosity under pressure). In that case, the velocity profile simplifies to a linear Couette flow

$$u(z) = \Delta U \frac{z}{h}. \quad (2.2)$$

Note that experimental conditions frequently deviate from the assumptions (1)-(4). For example, polymer solutions are known to exhibit slip under certain conditions [16]. Due to thermal effects, the viscosity might vary through the thickness of the film [17]. Experiments and numerical simulations have given evidence of deviations from Couette flows in EHD contacts. The solidification of the fluid in the contact due to high pressures leads to plug flow profiles [18, 19, 20, 21]. High pressures can also induce shear banding,

or shear localisation [22, 23, 24]. High shear promotes slip, and slip has recently gained more interest as it has the potential of increasing energy efficiency [25, 26]. Figure 2.3 shows possible flow profiles that can be observed in a contact under EHD conditions.

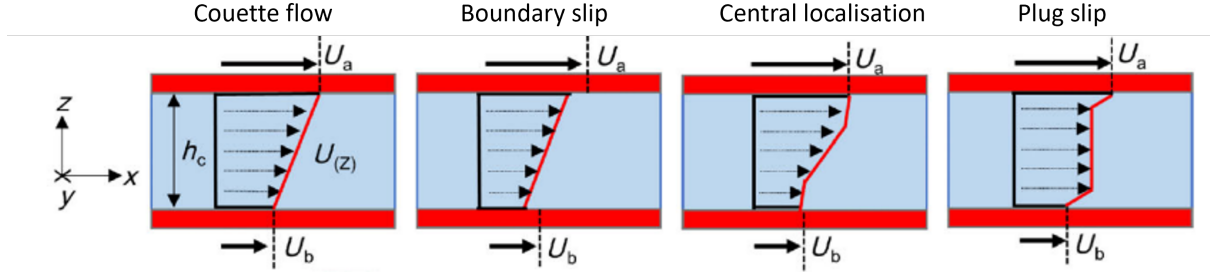


Figure 2.3: Some possible velocity profiles in a contact in the elastohydrodynamic regime, adapted from [27]

2.2.2 High-pressure viscometry

Engineering components such as bearings, gears, cams and other non-conforming contacts operating in the EHD regime can reach pressures in the range of 1-4 GPa [15]. Understanding the rheology of lubricants at very high pressure is necessary to improve fuel economy. Furthermore, friction losses in electric vehicles are also present from the transmission components, so studying the high-pressure response of lubricants continues to be highly relevant. The viscosity of a fluid increases significantly when under high pressures, and it is in practice very difficult to extrapolate results obtained at low pressures to predict the high-pressure response. Many models have been proposed to describe the viscosity-pressure relationship of a fluid. As reported by Dowson and Higginson in 1977 [28], they include exponential equations by Gatcombe, or by Winer, a parabolic equation by Hersey and Lowdenslager, and power laws by McEwen or by Roelands. The viscosity-pressure response of a lubricant is in its simplest form reduced to a single value, the viscosity-pressure coefficient α , where α is the coefficient in the so-called Barus equation

$$\eta = \eta_0 e^{\alpha P} \quad (2.3)$$

with P the pressure, η_0 and η the dynamic viscosity at atmospheric pressure and at pressure P , respectively. While equation 2.3 does not appear in Barus' work, he did study the relationship between viscosity and pressure via empirical observations of a thick oil, a marine glue [29]. He noted that in the range of pressure he studied (up to 200 MPa), the viscosity-pressure relationship was dependant on temperature, but not on pressure [29]. In fact, the viscosity response of lubricants does change significantly with pressure [30].

The best way to describe the viscosity-pressure behaviour of a fluid is still debated [31]. More accurate viscosity-pressure models have been since developed, as investigated in detail by Bair [32]. High-pressure viscometers such as capillary viscometers [33], diamond-anvil cell viscometers [34] and falling body viscometers [35, 36] have made possible the measurement of viscosity at very high pressures, and numerical simulations have advanced considerably and are now a powerful tool to estimate the viscosity-pressure relationship of lubricants with a good agreement with the experimental results [37, 38, 39, 40]. While now approaching conditions in the same range as EHD experiments, numerical studies are still limited by computational power, hence are restricted to small molecules and short timescales [27]. A thorough overview of high-pressure viscosity calculations using molecular dynamics simulations can be found in the recent review by Ewen *et al.* [41].

Some studies have specifically focused on the high-pressure viscometry of polymer solutions and viscosity modifiers-containing solutions. Bair [42] found that the response of a polymer solution to an increase of pressure depends on the polymer used. For example, the viscosity of a solution of polyisobutylene in mineral oil increases more than a solution of olefin copolymer in mineral oil when the pressure is increased [42]. Mary *et al.* [43] reported the viscosity-pressure relationship at high pressure, up to 800 MPa, of three different viscosity modifiers of different chemistries and architectures. They found that pressure has an effect on the solubility of the polymers. The hydrodynamic radius of polymers in a good solvent is almost unchanged by an increase of pressure, while it drops for polymers that are not in a good solvent [43]. For the three polymer solutions, they reported a good agreement for the viscosity-pressure dependence between the experimental data and the values calculated using the modified WLF-Yasutomi model (fit of the experimental data) [43].

2.2.3 EHD friction

Friction, also termed traction in this thesis, is of high importance in any tribological application as is at the heart of energy efficiency. Lubricants are designed to reduce friction over a wide range of conditions. A lower viscosity oil gives lower friction but the viscosity must be high enough to ensure adequate lubrication and limit wear. In a tribological point contact in the EHD regime, the friction depends (1) on the properties of the lubricant and its rheological response, (2) on the elastic deformation of the contact surfaces and (3) on the properties of the solid-liquid interface. In such a contact, the pressure distribution is approximated by Hertzian contact mechanics. Figure 2.4 shows the Hertzian pressure distribution in a point contact, along with the pressure distribution calculated by the numerical resolution of the EHD problem. The pressure distribution is not homogeneous, hence the viscosity and frictional responses are not homogeneous. The

coefficient of friction is maximum at the centre of the contact, where the pressure - hence the viscosity - is the highest. While friction is indeed not homogeneous in a tribological contact, the coefficient of friction measured via a friction test is given as a single value, dominated by the maximum friction in the contact.

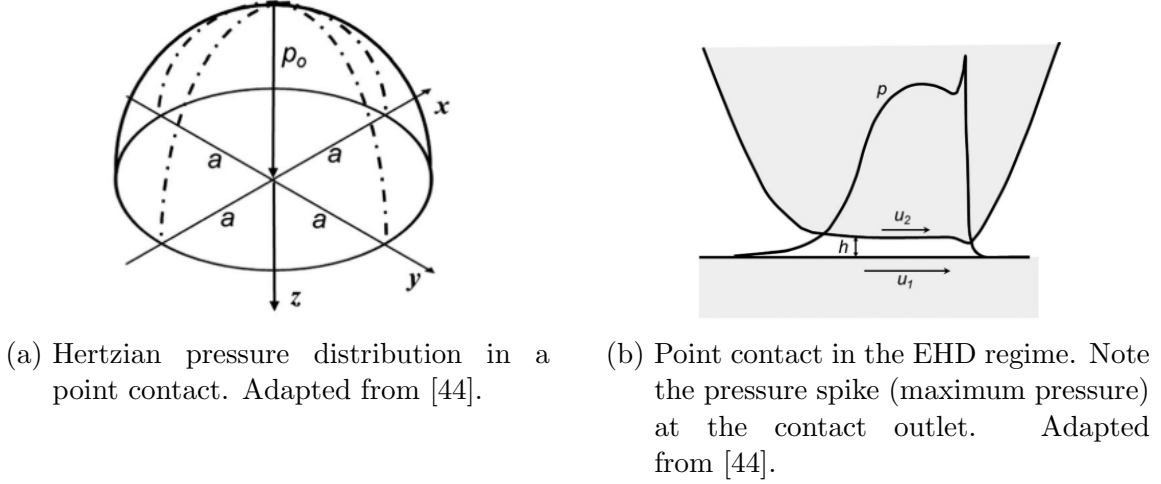


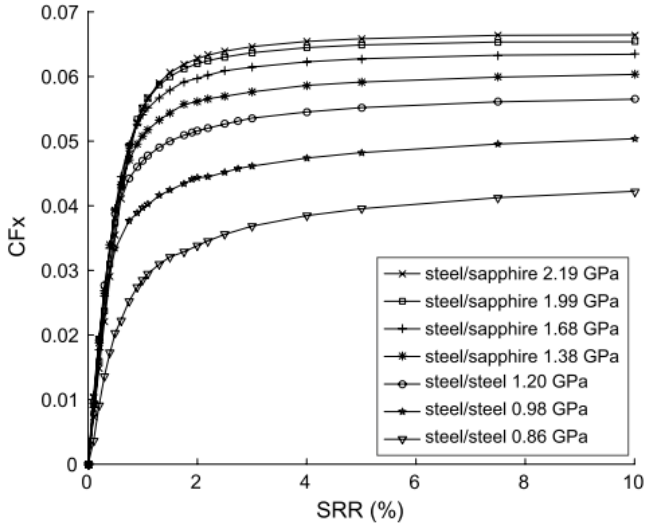
Figure 2.4: Pressure distribution of a point EHD point contact. (a) Hertzian pressure distribution prediction. (b) Pressure distribution from the numerical solution of the EHD problem.

Given that a viscosity distribution might exist, the conditions and the rheological response of a lubricant in the contact are poorly understood. The contact involves high pressure and high shear rate while the lubricant may experience shear thinning and shear heating. It is thus difficult to predict the friction accurately. The first models characterised the fluid as visco-elastic [45, 46]. Evans and Johnson [47] identified in 1986 different regimes of friction in the EHD regime, taking into account the shear-thinning behaviour and limiting shear stress: Newtonian, Eyring, viscoelastic and elastic-plastic. Viscoelastic effects can occur in lubricants at high shear rates, only when combined with a high pressure or a low temperature that make the relaxation time of the fluid equal or slightly longer than the time of passage through the contact [48]. When the relaxation time of the fluid is much longer than the time of passage of the fluid through the contact, elastic-plastic effects might occur [48]. More details on shear-thinning and the Eyring model will be given in section 2.7. The limiting shear stress is the value of shear stress above which the friction coefficient plateaus and any increase in shear rate does not lead to an increase in shear stress [49]. An example of friction curves reaching the limiting shear stress is shown in figure 2.5a. The mechanisms behind the existence of a limiting shear stress are still debated, and include either a glass transition of the fluid [50], interfacial slip of the fluid [48, 51], or shear localisation [52]. Not all fluids reach a limiting shear stress, even at very high pressures [15].

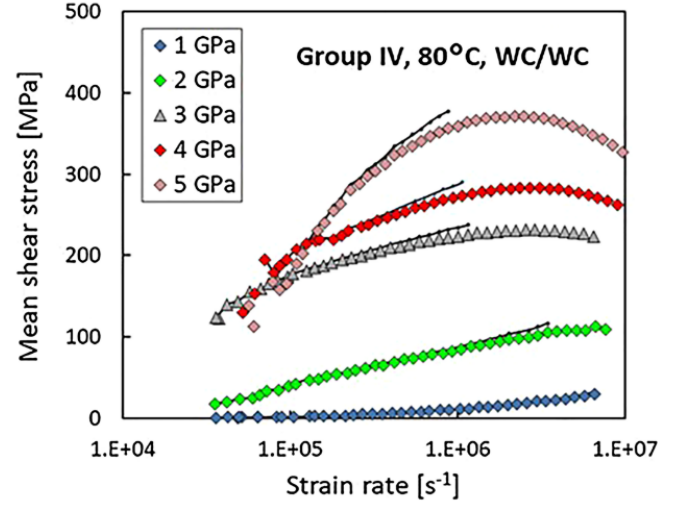
The friction models were then improved to include the thermal effects in the contact.

Shear heating leads to a reduction of friction. Due to the limitations in the thermal models, which typically involve analysis of heat transfer between moving sources and calculation of flash temperatures [53, 54], the isothermal corrections can only be done at low slide-roll ratios (SRR), where the temperature rise is relatively low. At higher temperature rises, the models are unreliable. Figure 2.5b shows an example of the difference in the mean shear stress before and after thermal correction.

In short, the tribological response is complex and difficult to predict, it depends on the properties of the fluid, the contact surfaces and the operating conditions. The pressure in an EHD contact has a major impact on the behaviour of the fluid.



(a) Coefficient of friction against slide-roll ratio for benzyl benzoate at $T = 313\text{ K}$, $U_e = 2.5\text{ m/s}$ at different pressures and specimen materials, adapted from [55].



(b) Mean shear stress against strain rate for a group IV base oil at 80 °C and different mean contact pressures. The black lines are values after the isothermal corrections, capped at a temperature rise of 10 °C . Adapted from [15].

Figure 2.5: Examples of frictional responses, limiting shear stress and isothermally corrected shear stress.

2.3 Lubricant composition

To improve the performance of lubricants, additives have been developed since the 1950s [7]. Lubricants are typically composed of a base oil with 5 wt% additives, and up to 15 wt% additives in some specific applications. Anti-wear additives react with contact surfaces and create a tribofilm that protects the surfaces in the boundary lubrication regime. Other additives such as anti-corrosion additives, anti-oxidants, detergents, pour point depressants, and anti-foam additives are some of the crucial components of fully formulated oils. Viscosity modifiers are additives that stabilise the viscosity of the oil

with temperature. Fully formulated oils are complex lubricants as additives are often multi-functional and can interact between themselves. Improving the performance of lubricants with better additives is therefore challenging but essential to improve the energy efficiency of engineering components.

Base oils are classified in five base stock groups by the American Petroleum Institute [56]. The mineral oil-derived base oils such as paraffinic base oils are in groups I, II and III, depending on how much sulfur they contain and their viscosity index. Polyalphaolefins (PAO) are in group IV, polyalkylene glycols, synthetic esters and polybutenes are in group V.

It is interesting to note that some fluids can be used both as base oils and additives. It is the case for polybutenes [57], and more recently esters have been seen as good candidates for electric vehicles, high viscosity esters as additives and thinner esters as base oils [58]. Fluids for electric vehicles have different requirements than fluids for combustion engines, such as conductivity, dielectric and thermal properties. They also need to limit copper corrosion and be able to withstand high voltages and high rotational speeds. Esters have been shown to perform well under these conditions, and have the advantage of being biodegradable, renewable materials [58, 59].

This work focuses on viscosity index improvers, also called viscosity modifiers. They are presented in more detail in the next section.

2.4 What are viscosity modifiers and how are they characterised?

Viscosity modifiers are used to thicken a fluid and reduce its change in viscosity with temperature. They are mainly used in engine oils but other applications include automatic transmission fluids, power steering fluids, gear oils, greases. By making oils less sensitive to temperature, they enable the development of lubricants that have a low viscosity at low temperature while retaining adequate viscosity at high temperature. Viscosity modifiers that reduce the temperature dependence of the oil are called viscosity index improvers, and viscosity modifiers that thicken the oil but do not impact its relative change with temperature are called thickeners.

2.4.1 Viscosity index

The efficiency of a viscosity index improver is given by the improved viscosity index of the VM-containing lubricant. The viscosity index is defined by the ASTM D2270 [60] as “an arbitrary number used to characterize the variation of the kinematic viscosity of a petroleum product with temperature”. The higher the viscosity index, the less the viscosity

changes with temperature.

The viscosity index is defined by equation (2.4) if $U > H$, where U is the kinematic viscosity of the oil at 40 °C, L and H the kinematic viscosities of two oils having the same kinematic viscosity at 40 °C as the studied oil and a viscosity index at 100 °C equals respectively to 0 and 100. The ASTM D2270 procedure gives L and H values for oils with a kinematic viscosity at 100 °C less than or equal to 70 mm²/s and describes the calculation method for all other cases.

$$VI = (L - U)/(L - H) * 100 \quad (2.4)$$

The viscosity index is commonly used to measure the quality of an oil and the performance of viscosity modifiers. As early as 1937, Bruson [61] patented the use of polymers as viscosity index improvers, and described the enhancement of the viscosity-temperature characteristics of an oil in terms of the viscosity index.

2.4.2 Mechanisms of polymeric viscosity index improvers

Selby [62] proposed in 1958 a theory to explain how polymers thicken and change the viscosity index of a base oil. He suggested that polymer molecules expand and therefore impact the viscosity, and that this mechanism depends on the quality of the solvent and on the blend temperature. The polymer molecules expand when the blend temperature increases. Consequently, a polymer-containing oil has a higher viscosity at high temperature than the base oil without polymer additives. In a good solvent, polymer molecules may expand even at low temperature, so they act as thickeners. Selby also highlighted one limit of the viscosity index: a polymer-containing oil that has a higher viscosity index than the base oil may not have a proportionately better viscosity-temperature dependence.

This mechanism is currently the most widely accepted. However, Müller [63] demonstrated in 1978 that the expansion of the polymer is not the only mechanism that explains the higher viscosity index of polymer blends. Naturally, if the polymer expands at high temperature, the viscosity index is higher for the oil containing the polymer than for the base oil. Nonetheless, in some cases, the size of the polymer coil is invariant with temperature. In 2015, Covitch and Trickett [64] confirmed, using small-angle scattering to measure polymer coil size, that a high viscosity index can be reached even when the polymer does not expand with a temperature rise. In that case, the viscosity of the base oil decreases at high temperatures while the contribution to viscosity of the viscosity modifier remains unchanged. The polymer thus contributes to maintaining a higher viscosity at higher temperature, leading to a higher viscosity index for the polymer solution than that of a base oil of similar viscosity.

Table 2.1 summarises the different mechanisms that have been proposed to explain how viscosity modifiers thicken the oil or change its viscosity-temperature relationship.

Table 2.1: Thickening mechanisms of viscosity modifiers

Proposed mechanism	Comments
Polymer molecules in a poor solvent expand when the temperature increases [62, 43]. As large molecules act to resist shear more strongly than small molecules, it increases the solution viscosity, while the solvent viscosity decreases with increasing temperature [62].	This mechanism is observed when the solvent is a poor solvent. The solvent quality increases with temperature: attractive interactions dominate between polymer segments at low temperature, then at higher temperature a globule-to-random coil transition takes place as the solvent becomes a good solvent. The transition temperature at which the polymer expands has to be in the range of temperatures experienced by the lubricant in the engine [64].
Polymer molecules do not expand significantly, or even contract, when the temperature increases [62, 63, 64].	Good solvent: polymer coils swell at low temperature [65]. The viscosity modifier acts as a thickener and not as a viscosity index improver [62].
No inter-molecular interactions between polymer molecules in the dilute regime [43].	In the dilute regime (low concentration), the polymer molecules are fully separated [43]. However, according to [66], this is the case only for extremely dilute solutions.
Polymer association [67], micelle formation [66].	Inter-molecular attraction and different solubilities to the solvent of the blocks of block copolymers leads to the formation of micelles [66].

2.5 Which polymer viscosity modifiers are commonly used?

At the beginning of the 20th century, rubbers and salts were used to raise the viscosity index. However, their performance was not satisfactory as they would degrade rapidly. Polymer additives have been presented since the 1930s as a better option to improve the viscosity-temperature relationship of lubricating oils [61]. Polymers are chosen for their performance as viscosity index improvers, for their cost, availability, easiness of composition change and control. Polymeric viscosity modifiers must be soluble in the oil, have good stability, be compatible with other additives, and have minimal environmental

impact [68]. A recent review by Martini [69] lists the polymers commonly studied and used as viscosity modifiers.

2.5.1 Polyacrylate polymers

Polyacrylates are polymer molecules having a great variety of architectures (linear, comb, star), backbone chain lengths and molecular weights (typically between 20000 and 750000 Da) [68]. Many studies from the 1930s to today underline that polymethacrylate polymers (PMA), polyalkylmethacrylate polymers (PAMA) and polyacrylate copolymers are good viscosity index modifiers, in a large range of average molecular weights and with different alkyl group side chains [62, 63, 70, 71, 72]. The chemical structures of PMA and PAMA are reported in figures 2.6 and 2.7. Polyacrylate polymers are synthesised from long-chain alcohols by esterification or transesterification [73]. PAMA polymers have the advantage that they can be used as dual additives, they were originally used as pour point depressants and gained interest more recently as friction modifiers [74] in addition to their use as viscosity modifiers. The use of viscosity modifiers as dual additives is investigated in more details in section 2.6.

Polyacrylate polymers are polar molecules whereas base oils are non-polar. Consequently, base oils are not good solvents for these molecules, PMA molecules collapse at low temperature and expand as the temperature is increased [43]. In engine lubricants, the concentration of PAMA is around 3 wt%, it is in the dilute regime at low temperature. This may not be the case at high temperature as a calculation by Mary [75] which gives a critical concentration (the concentration that separates the dilute regime from the semi-dilute regime) equal to 1.5 wt%. Consequently, PAMA would be in the semi-dilute regime at high temperature. PMA polymers are of particular interest nowadays as their architecture has a significant impact on the rheology of the solution containing the polymer, but the mechanisms behind these changes are not fully understood at the molecular level [43, 76].

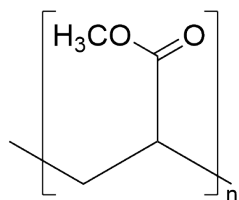


Figure 2.6: PMA

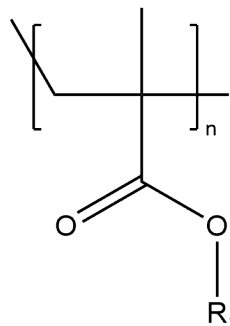


Figure 2.7: PAMA

2.5.2 Olefin copolymers (OCP)

Olefin copolymers (OCP) are commonly used as viscosity modifiers as they have a good balance between performance and cost. Base oils are good solvents for OCP as the latter are apolar. Due to this good affinity between OCP and base oils, temperature has a limited effect on the coil size [43]. Hence, OCP molecules act as thickeners and not as viscosity index improvers [65]. Figure 2.8 shows the chemical structure of OCP.

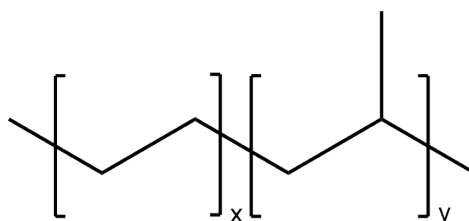


Figure 2.8: OCP

2.5.3 Other common viscosity modifiers

Styrene isoprene polymer (SIP) is a polar molecule used as a thickener. Polyisobutylene (PIB) is a thickener but is not used much nowadays as it does not have sufficient mechanical and oxidative stability [77]. Styrene butadiene (SBR) is also used as a thickener. The ratio of styrene and diene affects the polymer properties. Poly(isoprene-styrene hydrogenated) (PISH) are commonly used star-shaped viscosity modifiers.

2.6 Viscosity modifiers as dual additives

The use of multi-functional additives has been under active investigation for a couple of decades. The aim is to achieve friction reduction in the different regimes of lubrication. There is a growing interest in functionalised polymers which play the role of viscosity modifiers in the EHD regime and have the ability to adsorb on the surfaces and be effective friction modifiers in the boundary lubrication regime. In 1996, Smeeth *et al.* [78] measured the film thickness of solutions containing different viscosity modifiers and found surprisingly thick films at low speed, in the boundary regime. One of their results is reproduced in figure 2.9, showing a visibly thicker film at low speeds for some of the viscosity modifier solutions than for the base oil. This suggests that the polymer molecules are adsorbing on the rubbing surfaces and form a boundary film [78, 79]. The film forming capacity of polymeric viscosity modifiers depends on the molecular weight and architecture of the polymer [80].

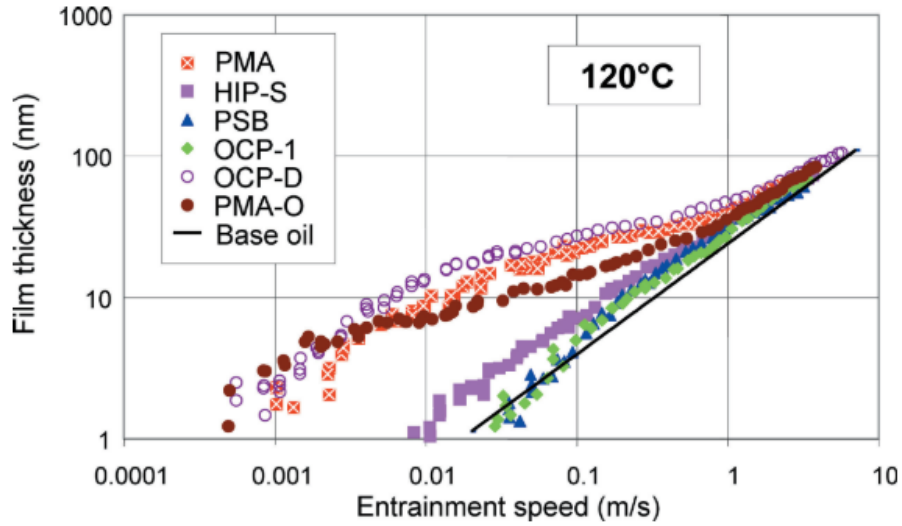


Figure 2.9: Film forming properties of viscosity modifier solutions in the boundary regime. Taken from [80], originally from [78].

More recently, the adsorption capacity of the viscosity modifiers have been enhanced by using block copolymers of appropriate functionalisation and anchoring blocks [81, 82]. These block copolymers are synthesised with a oil-soluble block and a polar block, the latter adsorbing on the surfaces to form mushrooms (low density packing) or brushes (higher density packing). Figure 2.10 shows the good performance of one of these polymeric friction modifiers (PFM) compared to glycerol monooleate (GMO), a commercially used organic friction modifier.

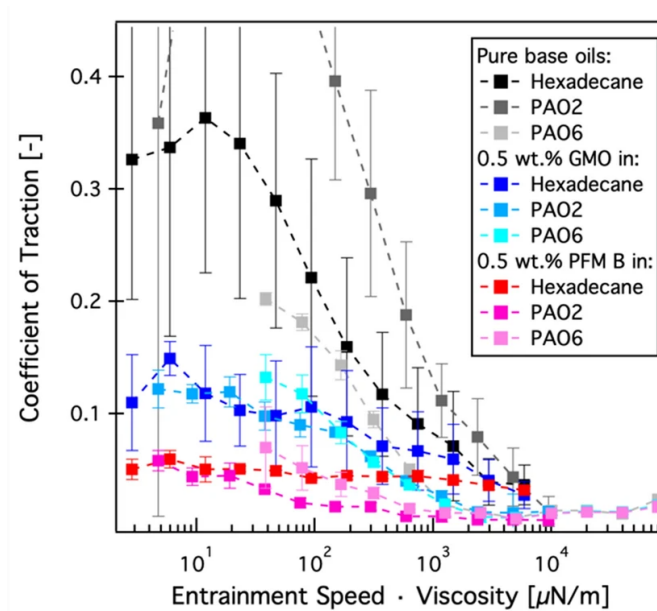


Figure 2.10: Friction performance of a block copolymer (PFM B) in different base oils, at 30 °C, adapted from [82].

2.7 Shear dependence of polymer-containing oils

2.7.1 Shear stability

Polymers are effective viscosity modifiers; however, their behaviour may be altered under high shear conditions. Shear-thinning, which is a reduction of the effective viscosity at high shear stress, can be temporary, or permanent when the molecules break and the viscosity of the sheared oil does not return to its initial value and remains lower [62]. The ASTM standards D5275 [83] and D6278 [84] define the permanent viscosity loss (PVL) by equation (2.5), where V_u is the kinematic viscosity of the unsheared oil at 100 °C and V_s the kinematic viscosity of the sheared oil at 100 °C.

$$PVL = 100 * (V_u - V_s)/V_u \quad (2.5)$$

To isolate the contribution of an additive in the viscosity loss, the permanent shear stability index (PSSI) is used [85]. Equation (2.6) is valid if the ratio between the viscosity of the unsheared oil and the viscosity of the base oil is greater than 1.2. V_u , V_s and V_b are the kinematic viscosities of, respectively, the unsheared oil, the sheared oil and the unsheared base oil under the same temperature and shear stress conditions.

$$PSSI = 100 * (V_u - V_s)/(V_u - V_b) \quad (2.6)$$

The temporary shear stability index is calculated using the same equation (2.6) in which the final sheared viscosity is replaced by the viscosity at a given shear rate.

In 1958, Horowitz [86] measured the viscosity loss resulting from shear stress of polybutene and polymethacrylate oils. The author found that the viscosity loss depends on the polymer and on temperature. The temporary shear-thinning of polybutene is presented by Horowitz as a benefit as it makes easier and more fuel efficient the start of cold engines than it would be without this loss in viscosity. Now, more than ever before, reducing friction in engines is crucial. By designing appropriate shear dependent polymer-containing oils, shear-thinning can be used as an effective way of improving engine efficiency.

Stambaugh and Kopko [87] investigated this non-Newtonian behaviour. They showed that for a given polymer –in their case polymethacrylate –the viscosity loss is higher with higher molecular weight molecules.

2.7.2 Shear-thinning mechanisms

When shear stress is applied, polymer molecules align in the direction of the flow, resulting in temporary shear-thinning [62]. Permanent shear-thinning is caused by

polymer molecule breakdowns [62]. Different techniques were developed to study shear-thinning and results support these mechanisms. Cann and Spikes [88] used an infrared spectroscopy technique at the inlet of a tribological contact. They found relatively more in-plane vibrations than out-of-plane vibrations when the fluids were sheared, concluding that molecules align in the inlet, and linking it to the viscosity loss of the fluid. Lee and Muller [89] used light scattering to investigate the behaviour of polymer molecules (dilute solutions of polystyrene in different solvents, such as phthalate esters) under shear. They observed that under shear, the polymer chains in a poor solvent align more in the direction of the flow than when in a good solvent.

High molecular weight molecules are more vulnerable to degradation [90, 91]. For a given shear rate, the viscosity reaches a plateau once all chain scissions have taken place [92]. The initial viscosity before shearing is referred as the first Newtonian viscosity, and the viscosity after shear-thinning is the second Newtonian viscosity. Figure 2.11 illustrates the shear-thinning behaviour of a polymer solution. Molecular weight is not the only factor playing a role on the extent of permanent shear-thinning. Ghosh *et al.* [91] showed that it is influenced by the viscosity of the base oil, polymer concentration, and base oil composition. Marx *et al.* [93] confirmed that permanent shear-thinning is driven by shear stress (rather than strain rate) and extended the analysis using an ultrashear viscometer (USV). They showed that for polystyrene additives, the extent of permanent shear-thinning varies linearly with polymer concentration and exponentially with shear stress.

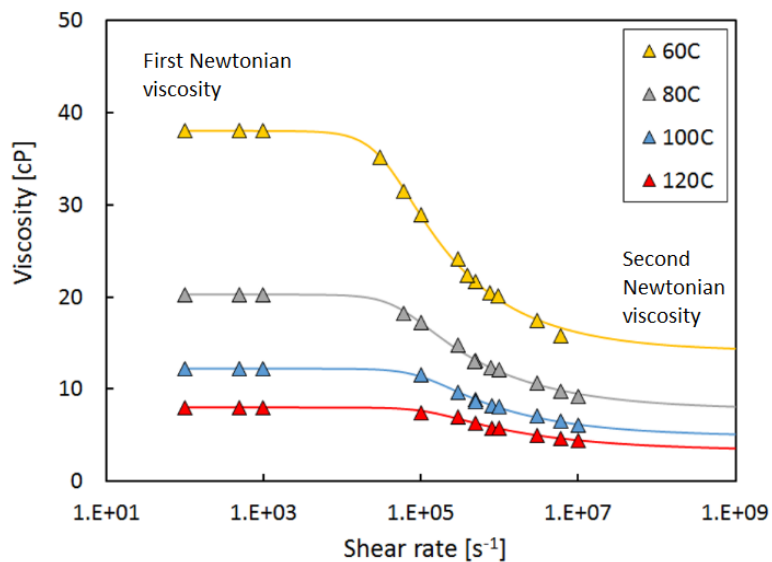


Figure 2.11: Flow curve of a polymer solution (Group II base oil + 13.5 wt% OCP), adapted from [94].

2.7.3 Shear-thinning models

Several models and equations exist to describe the shear-thinning behaviour of a fluid. The reader can refer to the review on elastohydrodynamic friction by Spikes and Zhang [95] and to a recent paper by Ewen, Spikes and Dini [41] for details on the uses and limitations of the two main models, the Eyring model [96] and the Carreau model [97]. The corresponding equations are, for the Eyring model,

$$\tau = \tau_e \operatorname{asinh}\left(\frac{\eta\dot{\gamma}}{\tau_e}\right) \quad (2.7)$$

where τ is the shear stress, τ_e the Eyring shear stress, $\dot{\gamma}$ the shear rate and η the low-shear dynamic viscosity of the fluid, and for the Carreau model,

$$\tau = \frac{\eta\dot{\gamma}}{(1 + (\lambda\dot{\gamma})^2)^{(1-n)/2}} \quad (2.8)$$

where λ and n are two constants.

In short, in the Eyring model, the shear stress τ increases linearly with the logarithm of the shear rate $\log(\dot{\gamma})$ at high shear rates. This model is valid when $\tau > 2\tau_e$. In the Carreau model, the relationship between the shear stress τ and the shear rate $\dot{\gamma}$ is a power law.

2.8 Rheology of dilute polymer solutions

2.8.1 Polymer solutions

Polymers are characterised by their degree of polymerisation, which is the number of monomers in the polymer molecule, by their architecture (linear, star, comb for instance), and their conformation. For heteropolymers, additional key parameters are the composition (monomers that compose the polymer molecule) and the sequence (alternating, blocks, random). All these intrinsic attributes give particular thermal and mechanical properties to the polymer.

The behaviour of polymer molecules is also dependent on external factors such as temperature, shear rate, pressure and concentration, and solvent properties when they are in solution [98]. Polymer solutions are defined as polymers dissolved in a solvent, by contrast with polymer melts. Polymer solutions are dilute at low volume fraction and semi-dilute when the volume fraction is above the overlap volume fraction. The overlap volume fraction is reached when the polymer molecules overlap. Physical properties of dilute solutions are dominated by the solvent but impacted by the polymer molecules. The solvent quality has an impact on polymer behaviour. In the dilute regime, polymers

collapse in a poor solvent, they behave as ideal chains in a theta solvent and they swell in a good solvent [98]. Solvent quality decreases with decreasing temperature. A polymer chain is ideal when interactions between monomers can be neglected.

This multiplicity of parameters makes the prediction of the polymer response difficult.

2.8.2 Effect of architecture on shear response

The study of polymer molecules under shear flow is of interest as, while shear flows such as Couette flows are common and well documented, systems such as polymer solutions exhibit complex flows and the dynamics of sheared polymers is not fully understood. Nowadays, it is possible to investigate polymer behaviour at the molecular level with fluorescence imaging. Large molecules such as DNA molecules are labelled to allow single molecule observations, and in a steady shear flow these molecules do not simply stretch but exhibit a more complex behaviour, they can coil, fold, or take a U-shape [99].

Behaviours of polymers of various architectures are studied, the most common architectures are given in figure 2.12. The polymer architecture impacts the extent of shear thinning undergone by polymer solutions subjected to high shear rates. Comparisons between molecules of different architectures are not straightforward as many parameters are interlinked, such as the molecular weight, the hydrodynamic radius, the degree of branching and the length of arms. They all play a role in the shear response and there is little agreement in the literature about the effect of these different parameters.

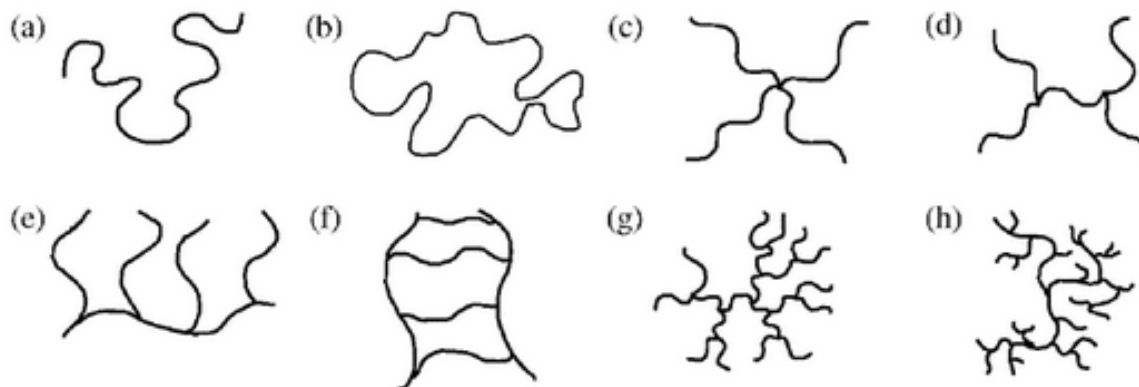


Figure 2.12: Types of polymer architecture (a) linear, (b) ring, (c) star, (d) H, (e) comb, (f) ladder, (g) dendrimer, (h) randomly branched, adapted from [98].

Concerning the branching of polymers, some studies showed that this has a great impact on the shear response of polymer solutions. Highly-branched polymers exhibited non-Newtonian shear-thinning behaviours at lower shear rates, and to a greater extent, than less branched polymers. This was studied as early as 1965 for polybutadiene

molecules of different molecular weights [100], and later for polyacrylamide molecules of different number of arms but equal molecular weight [101]. However, in a recent study on methacrylate polymers, Cosimbescu *et al.* [76] stated that polymer architecture, more particularly the number of arms for hyperbranched star polymers, has a minor effect on shear stability compared to the impact of molecular weight on shear stability. They found that shear stability is mainly driven by molecular weight. In their work, some linear polymers and branched polymers of similar molecular weight have the same shear stability behaviour. They used branched polymers with long arms and studied them at high temperature and under shear, which may explain the discrepancy between their results and those previous studies that used shorter polymer arms.

Comparing different architectures, no difference has been observed in the rheology between linear and star-shaped branched polymers, meaning the values of the low-shear viscosity can be derived from the same model regardless of the polymer structure (linear or star-shaped) [102]. However, at high shear rates, the branching does have an effect on the shear response, but this is still debated. Eckert [103] patented in 1977 star-shaped polymers having between 7 and 15 arms for their excellent efficiency as viscosity index improvers while showing less permanent and temporary shear-thinning than the linear viscosity index improvers used at that time. Molecular dynamics simulations of polymers of different molecular structures and equal molecular weight have found that comb polymers shear thin the least, and star-shaped polymers have a better shear stability than those with a linear architecture [104]. A proposed mechanism supporting these results is that temporary shear-thinning might be driven by the flexibility of the polymer molecules [43, 65] and by their size [65]. Comb and star molecules have intra-molecular interactions between their branches, which make the polymer chain less flexible, preventing chain deformations hence limiting shear-thinning [43]. This is contradicted by a study by Wever *et al.* [101] which shows that star polymers with 13 and 17 arms display more shear-thinning than the linear molecule of equal molecular weight. Note that Wever *et al.* [101] compare polymers of different architectures but of similar chemistry, all the polymers tested were polyacrylamide molecules, while Mary *et al.* [43] use different chemistries for each architecture: PMA for comb, OCP for linear, and PISH for star.

Another molecular dynamics simulation study by Kioupis and Maginn [105] brings interesting insights on the mechanisms behind shear-thinning for the different polymer architectures. They simulated and compared the rheology of linear, star and highly-branched PAO isomers of similar molecular weight and degree of polymerisation (18 atoms of carbon). They found that the highly-branched isomer has the highest viscosity at all shear rates. The star isomer has the lowest viscosity at low shear rate but, because of shear-thinning, the linear molecules end up with the lowest viscosity

at high shear rates. They also found that star molecules shear-thin less and at higher shear rates than linear and highly-branched molecules. The latter two exhibit a similar shear-thinning behaviour. However, while shear-thinning is caused by molecular alignment for the linear molecules, the mechanism appears to be different for the highly-branched molecules. Highly-branched molecules do not align as easily in the direction of the flow as linear molecules, and their shear-thinning behaviour may be due to a reduced number of interchain contacts under sliding, due to their globular nature.

2.9 Film thickness of polymer solutions

The film thickness of polymer solutions is fundamental from a tribological viewpoint as it determines the quality of the lubrication, from wear when too low to high friction when too high. Due to its complexity, the film thickness of polymer solutions is of particular interest. In this section, the conventional models for the film thickness are first reported, then the deviations due to the presence of polymers in the base oil are presented.

2.9.1 Conventional models for EHD film thickness

Several models have been proposed to predict the film thickness in an EHD contact. Only the models most relevant to this work are presented here, an exhaustive list of the equations with the corresponding conditions of use can be found in [106]. The equations for the central film thickness h_c from the Hamrock & Dowson, and Chittenden *et al.* are the following for a circular contact:

$$\text{Hamrock \& Dowson [107]:} \quad h_c = 1.91 R_x \bar{U}^{0.67} \bar{G}^{0.53} \bar{W}^{-0.067} \quad (2.9a)$$

$$\text{Chittenden } et al. [108]: \quad h_c = 3.05 R_x \bar{U}^{0.68} \bar{G}^{0.49} \bar{W}^{-0.073} \quad (2.9b)$$

where R_x is the reduced radius of curvature in the entrainment direction, and $\bar{U}$, $\bar{G}$ and $\bar{W}$ are respectively the dimensionless speed, material and load parameters given by

$$\bar{U} = \frac{\eta U_e}{E^* R_x} \quad (2.10a)$$

$$\bar{G} = \alpha^* E^* \quad (2.10b)$$

$$\bar{W} = \frac{W}{E^* R_x^2}. \quad (2.10c)$$

η is the dynamic viscosity, U_e the entrainment speed, W the normal load, E^* the reduced modulus of elasticity, and α^* the pressure-viscosity coefficient as defined by Blok (also called the reciprocal asymptotic isoviscous pressure by Bair [109]).

The validation of these models was provided by the development of experimental techniques to measure the central film thickness, such as the optical interferometry

technique [110]. However, in the case of complex fluids or extreme operating conditions, the central film thickness calculated with the conventional models deviates from the values measured experimentally. An example adapted from [111] with the very high molecular weight polyalphaolefin PAO-650 is given in figure 2.13. The film thickness obtained with Hamrock & Dowson equation (equation 2.9a) is overestimated as the fluid shear thins.

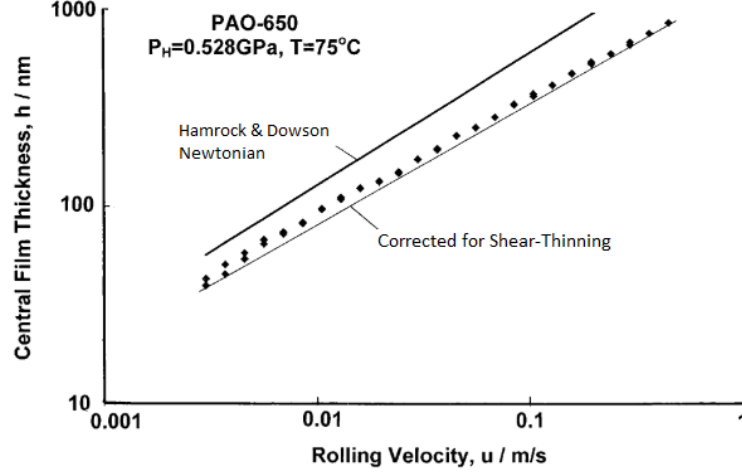


Figure 2.13: Central film thickness of PAO-650, comparison between calculation from Hamrock & Dowson (equation 2.9a) and experimental data, adapted from [111].

2.9.2 Effect of shear-thinning on the film thickness of polymer solutions

The viscosity of a polymer solution experiencing shear-thinning drops. This raises the question of how a drop in viscosity impacts the film thickness, as the latter is viscosity dependant, keeping in mind that the viscosity which drives the film thickness is the inlet viscosity [112]. For a tribological contact under high shear, the fluid experiences a shear rate of about 10^6 s^{-1} at the inlet [95]. Usually, polymer solutions start shear thinning at shear rates lower than 10^6 s^{-1} . Marx *et al.* [113] studied VM solutions and found an onset of viscosity drop at shear rates between 10^4 s^{-1} and 10^5 s^{-1} . Habchi *et al.* [114] reported shear thinning of a solution of polyisoprene in squalane from 10^3 s^{-1} . It is thus difficult to predict the film thickness of polymer solutions as the viscosity at the inlet drops due to shear-thinning. Calculations done with conventional EHD equations and using the viscosity of the solution at low shear rate overestimate the film thickness. However, Bair [115] found that when using the value of the second Newtonian viscosity instead of the first Newtonian viscosity in the models, the predicted film thickness matches well the measured values.

2.9.3 Effect of slip on the film thickness of polymer solutions

Another phenomenon that has an effect on film thickness is slip. The film thickness in the contact depends on the velocity profile and the location of the slip. The conservation of mass implies that a change in the mean velocity of the lubricant in the contact is necessarily linked to a change in film thickness. Ponjavic and Wong [116] showed that interfacial slip in an EHD contact leads to a reduction in film thickness and, at high pressure, in friction. Wang and Reddyhoff [117] found, for 1-dodecanol, that the film thickness increases when slip occurs near the faster contact surface, and decreases when slip occurs near the slower contact surface, in order to maintain flow continuity. If slip occurs within the film, at the midpoint, the film thickness does not change. Interestingly, they also linked slip to friction reduction. Slip can occur for polymer systems due to the different affinities between the contact surfaces and the polymer molecules or the solvent. When the polymer molecules move away from the walls, a thin layer depleted of polymer molecules is created by the wall [118]. This thin layer of lower viscosity might promote lower friction [119]. The polymer molecules can in some cases adsorb on the contact surfaces and promote slip through a different mechanism: the layer of adsorbed molecules alter the chemical properties of the surface, inducing a change for the boundary conditions and for the velocity profile in the contact [120].

2.9.4 Other effects affecting the film thickness of polymer solutions

As the film thickness is driven by the conditions at the inlet of the tribological contact, it might be impacted by the accumulation of polymer molecules or their adsorption on the contact surfaces. Yoshida *et al.* [121] found that for solutions of PMA of different molecular weights but of same bulk viscosity, the film thickness increases with decreasing molecular weight. The base oil of same viscosity has the highest film thickness. They suggested that the large molecules of PMA might accumulate at the inlet, blocking oil supply, or sweep around the contact instead of passing through it, whereas small molecules of PMA (low molecular weight) might pass easily through the contact [121]. This would need to be confirmed with further research as an accumulation of polymer molecules at the inlet would increase the viscosity at the inlet, hence lead to an increase in the film thickness, not a decrease. Moreover, with a relatively similar system of PMA solutions and using interferometry and infrared spectroscopy, Wardle *et al.* [122] detected polymer molecules in the tribological contact and their results suggest that the polymer molecules were shear-thinning at the inlet, leading to a reduction in film thickness. These questions are still debated as the local mechanisms in the EHD tribological contact are yet to be fully understood.

2.10 Bridging the gap of knowledge between macro- and micro-scale phenomena

Despite the numerous studies on polymer solutions and viscosity modifiers, there are still gaps in knowledge about their fundamental mechanisms in a tribological contact, about the link between their chemical structure and the rheological and frictional responses of the lubricant, and more generally about their behaviour across scales. This chapter has highlighted the close relationship between the nature and structure of polymers and the rheological response of the polymer solutions. The shear and pressure responses are directly related to polymer properties such as chemistry, architecture, molecular weight and concentration.

Concerning the tribological response, it is clear that polymers impact the film thickness, at low speed by adsorbing on the contact surfaces (see section 2.6) and at high speeds by shear thinning. What is harder to assess is the role of polymers in the frictional response of a polymer solution in the elastohydrodynamic regime. What is already known is that the friction of base oils is indeed impacted by the structure of the molecules. Zhang *et al.* [123] measured the EHD friction of 38 fluids among which were base oils, polyalphaolefins (PAO) and a polyisobutylene (PIB). They found that the molecular structure of the fluid has a strong effect on friction, with linear-shaped molecules with flexible bonds giving lower friction than fluids having bulky side groups or rings. They also demonstrated that small differences in the molecular structure can have a significant impact on friction. Knowing this, it is most likely that adding viscosity modifiers or more generally polymers to a base oil would impact the frictional response. Marx *et al.* [94] investigated the friction of several polymer solutions and found a lower friction for the polymer solutions than for the reference base oil. Comparing the different solutions, they suggested that the friction reduction is due to both shear-thinning and an increase in the viscosity index. Comparing two oils of similar viscosity at high temperature but of different viscosity index, the oil with the highest viscosity index has a lower viscosity at lower temperatures, and consequently a lower hydrodynamic friction, than the oil with the lowest viscosity index. The authors did not comment on the role played by the chemical structure of the polymers, but as explored in this chapter, shear-thinning and a change of viscosity index are highly dependent on the molecular structure of the polymers. It should also be noted that their study was conducted in the hydrodynamic lubrication regime. In this regime, it is easier to identify differences due to a larger volume of fluid being entrained into the contact compared to the elastohydrodynamic regime. Mary [75] investigated the film thickness and friction of three polymer solutions, PAMA, OCP and PISH in a group III mineral base oil. She found that the film thickness was impacted differently by the three polymers, due to shear-thinning, with a higher drop

in film thickness for the PISH solution than for the OCP solution. The PAMA solution has the lowest decrease in film thickness. She concluded that the more shear-thinning, the larger the deviation of the film thickness from the theoretical predictions. However, she surprisingly found a similar coefficient of friction for the three solutions and for the base oil, for the range of SRR studied (0 % to 50 %). She cautiously concluded that the frictional response might be governed by the base oil [75]. At SRR as high as 50 %, it is likely that the polymer solutions shear thin, leading to a drop in friction, but this decrease might be compensated by the increase of viscosity provided by the polymers, giving an overall similar friction to the base oil. In this work, the increase of the kinematic viscosity (low shear and atmospheric pressure) after addition of the polymer was 9 %, 116 % and 131 % at 40 °C and 18 %, 96 % and 112 % at 100 °C for PAMA, OCP and PISH, respectively. The PISH solution had the highest kinematic viscosity.

2.11 Summary and objectives

The state-of-the-art related to the scope of this thesis has been presented. The rheology of confined solutions in the elastohydrodynamic regime is not fully understood, especially in the more complex case of polymer solutions.

Under high shear and high pressure, the behaviour of lubricants is non-Newtonian in most cases. Fluids under severe conditions exhibit velocity profiles that deviate from a Couette flow. Possible velocity profiles include shear localisation, plug flow and slip, the latter being of particular interest in the case of polymer solutions.

Spatial heterogeneity means information on the local behaviour of the fluid in the tribological contact is needed. The pressure in an EHD contact is a Hertzian distribution, driving spatial variations of viscosity in the contact. The viscosity-pressure response of lubricants is still under investigation and debated in the literature, in particular at high pressures.

The shear response of lubricants is discussed at length. Interest is placed on shear-thinning as a potential way of reducing friction, hence increasing energy efficiency. The shear response of polymer solution is complex as is driven by many parameters, such as polymer architecture, chemistry and molecular weight, goodness of the solvent, concentration, among other factors.

A better understanding of the rheology of fluids in an EHD contact, across scales, is necessary to improve the design of lubricants, enhance their lubrication performance and the energy efficiency of engineering systems.

The objectives of the research described in this thesis are:

- Investigate the rheological behaviour of polymer solutions in the elastohydrodynamic lubrication regime. Explore, for different polymer and copolymer solutions, the shear-thinning and adsorption responses and assess their impact on film thickness and velocity profile.
- Probe the presence of polymer molecules in an EHD contact to assess if polymer molecules enter the contact or not. Quantify the composition of polymer solutions at the inlet and in the contact to examine polymer depletion, aggregation or other possible mechanisms.
- Develop a methodology to link friction performance and high-pressure viscometry of lubricants. Propose models to predict the viscosity-pressure relationship based on standard friction and film thickness tests.

Chapter 3

Materials and methods

This chapter describes the rigs and experimental methods used in this work to obtain the rheological and tribological responses of fluids. Conventional rigs are used for the measurement of the film thickness, friction coefficient, low-shear and high-shear viscosity. A modified rig is developed to obtain the mid-shear viscosity. Spectroscopy techniques enabling local measurements in EHD contacts are reviewed. The focus is on fluorescence anisotropy, fluorescence lifetime spectroscopy and Raman spectroscopy.

3.1 Film thickness measurements using interferometry

Optical interferometry has been used for decades for the measurement of EHD film thickness in tribological contacts [124]. This technique can now be used for film thicknesses down to 1 nm [125]. In this work, the central film thickness is measured using an EHD2 rig by PCS Instruments (Acton, UK). The contact comprises of a steel ball, immersed in a lubricant bath, loaded against a glass disc. The material properties of the disc and the ball are listed in table 3.1. The disc is coated with a thin chromium layer and a silica spacer layer to create interferences, as it splits the light into two optical paths of different lengths. Part of the light is reflected on this layer of coating and part of the light goes through the thin film of lubricant and is reflected on the steel ball [124]. The film thickness is then calculated from the wavelengths of the constructive interferences. The ball and the disc are independently driven by two motors, the speed and slide-roll ratio are controlled. The load applied on the ball, and the temperature of the fluid are also controlled. An example of the central film thickness measured with the EHD2 rig is given in figure 3.1 for bis(2-ethylhexyl) sebacate (DEHS) at different temperatures. As expected for this relatively thin ester, the film thickness increases linearly with speed in the log-log plot, and decreases with temperature.

Table 3.1: Material properties of specimens used in film thickness measurements with the EHD2

Material	Elastic modulus E (GPa)	Poisson's ratio ν
Glass	75	0.22
Steel	207	0.29

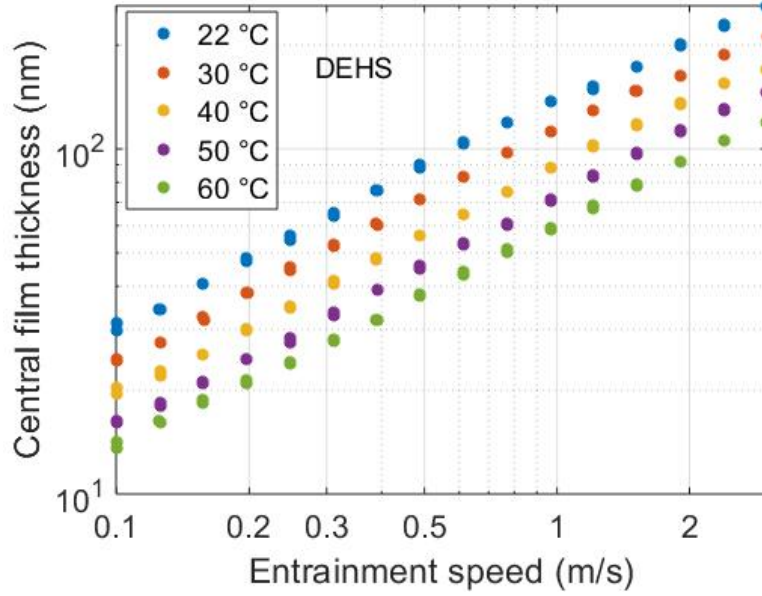


Figure 3.1: Central film thickness of DEHS at different temperatures, with pure rolling conditions and the steel ball loaded (20 N) against the glass disc.

3.2 Friction measurements

The friction was measured experimentally using a mini-traction machine (MTM) by PCS Instruments (Acton, UK). The tribological contact is created by loading a ball against a disc fully immersed in a bath of lubricant. The ball and the disc are independently driven by two motors, so the rolling and sliding speeds are controlled. To eliminate rolling friction, each data point is an average of two measurements: a positive and a negative slide-roll ratio (ball moving faster or slower than the disc, respectively). The specimens are commonly made of AISI 52100 steel but other materials can be used to access a wider range of pressures or to change the thermal conductivity of the contact surfaces. The temperature is controlled by a close loop system. The friction force is measured by a force transducer mounted on the ball shaft.

3.3 Viscosity and shear thinning characterisation

To characterise shear thinning, the viscosity of the fluids are measured over a wide range of shear rates, from 10^1 s^{-1} to 10^7 s^{-1} , using different viscometers described in the following sections.

3.3.1 Low-shear viscometry

The dynamic viscosity at low shear rate is measured with a Stabinger viscometer SVM-3000 (Anton Paar). The measuring cell is composed of a outer cylinder and an inner rotor and viscosity measurements are based on the rotational speed of the rotor. The shear rate in the Stabinger viscometer is estimated to be between 10^1 s^{-1} and 10^3 s^{-1} [126], which is low enough to assume that the tested fluids used are not experiencing any shear-thinning during the viscosity measurement.

The dynamic viscosity can be measured at different temperatures with the Stabinger viscometer. The viscosities at 40 °C and 100 °C are used to calculate the viscosity index of the fluid, which is of particular interest for polymer solutions.

The decrease of viscosity with temperature is described by the Vogel equation

$$\eta = Ae^{\frac{B}{T-C}} \quad (3.1)$$

where η is the dynamic viscosity, T is the temperature and A , B and C are three constants.

An example of data points obtained with the Stabinger and the fit using the Vogel equation is given in figure 3.2. The fluid is a phthalate ester, dibutyl phthalate.

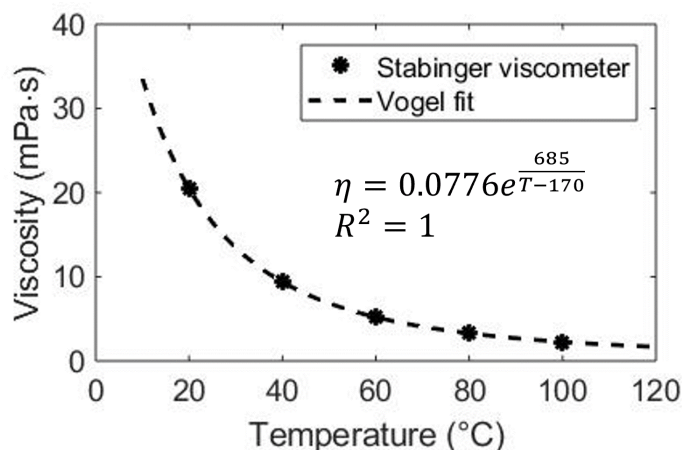


Figure 3.2: Viscosity of dibutyl phthalate

3.3.2 High-shear viscometry

The high shear viscosity is measured with a USV (Ultra Shear Viscometer) by PCS Instruments. The range of shear rate is 10^6 s^{-1} - 10^7 s^{-1} and the range of temperature is $40 \text{ }^\circ\text{C}$ - $150 \text{ }^\circ\text{C}$. The fluid is sheared between two cylinders, an outer stator and an inner rotor. The gap between the stator and the rotor is fixed at approximately $1.3 \text{ }\mu\text{m}$. When measuring the viscosity, the USV estimates the temperature rise due to shear heating and compensates for it by slightly reducing the temperature of the measuring cell. Each data point is the average of three repeats. The main limitation of the USV is its limited maximum torque. Only fluids with a viscosity low enough that would not make the torque exceed its limit could be tested.

3.3.3 Mid-shear viscometry

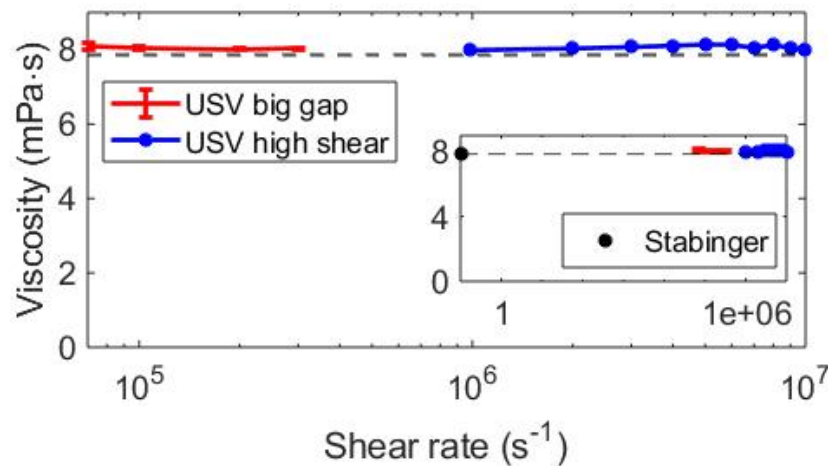
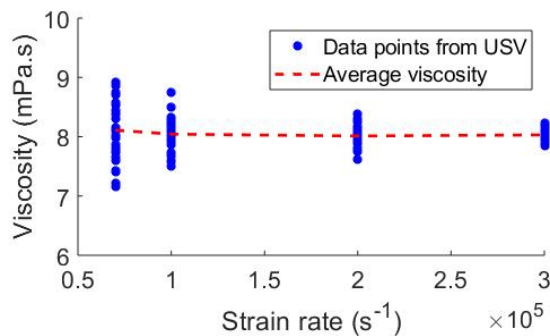


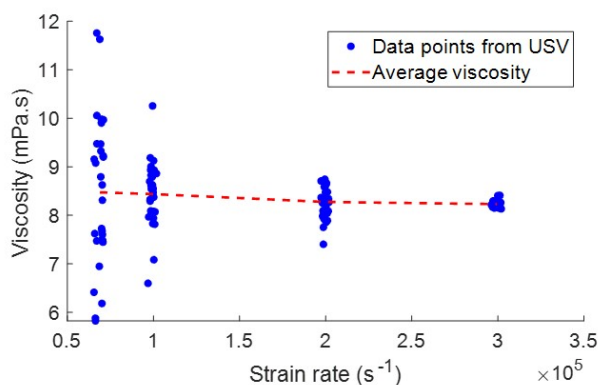
Figure 3.3: Flow curve for squalane, at $60 \text{ }^\circ\text{C}$. Black dotted line represents low shear viscosity value. Insert shows all data points at low shear rate (Stabinger viscometer), medium (big gap configuration) and high shear rates (USV standard configuration).

Some of the fluids in this study start to shear thin at shear rates lower than 10^6 s^{-1} , another viscometer is hence needed to extend the flow curves to lower shear rates. Consequently, the USV was adapted to reach lower shear rates, in the range of $7 \times 10^4 - 3 \times 10^5 \text{ s}^{-1}$, following the work done by Marx [126, 113]. The rotor and stator specimens were changed to increase the gap. After calibration, the new gap was found to be $5.25 \text{ }\mu\text{m}$. Calibration was performed using squalane, as this fluid has a Newtonian response with no shear thinning, even for the highest shear rate of 10^7 s^{-1} . The flow curve at $60 \text{ }^\circ\text{C}$ for squalane is shown in figure 3.3. The viscosities measured with the big gap configuration are very satisfactory and match the viscosity measured with the USV under standard high shear conditions. Each data point generated from the big gap configuration

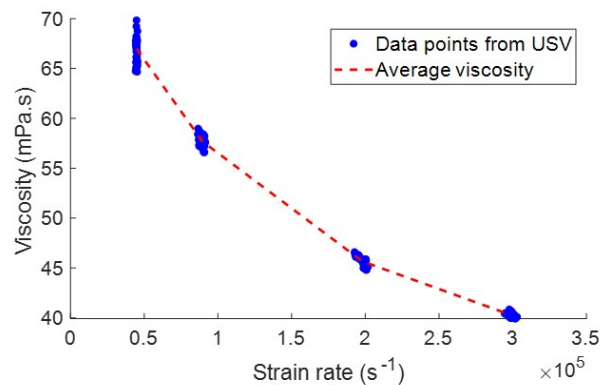
is an average of thirty repeats. Note that viscosity values at medium and high shear rates are slightly higher than the reference data, the low shear value measured with the Stabinger viscometer (dotted line in figure 3.3). The difference in viscosity between the low shear viscosity and the high shear viscosity is 2.6 % and is 2.4 % between the low shear viscosity and the mid-shear viscosity. These very small deviations confirm the very satisfactory results of the mid-shear configuration of the USV.



(a) squalane



(b) dibutyl phthalate + 3.2 wt% polystyrene ($M_w = 35 \text{ kDa}$)



(c) dioctyl phthalate + 10 wt% polystyrene ($M_w = 192 \text{ kDa}$)

Figure 3.4: Viscosity of (a) squalane and (b,c) two polymer solutions measured using the big gap configuration of the USV

Figure 3.4 shows viscosity measurements at different shear rates for squalane and two polymer solutions, a thin dibutyl phthalate + 3.2 wt% polystyrene ($M_w = 35 \text{ kDa}$) solution and a more viscous dioctyl phthalate + 10 wt% polystyrene ($M_w = 192 \text{ kDa}$) solution. Squalane and the first polymer solution do not undergo shear thinning at these shear rates as the viscosity is constant, while the other polymer solution, which contains a polymer of higher molecular weight, experiences a viscosity loss as the shear rate increases. In all cases, the standard deviation of the 30 data points improves considerably with increasing shear rate. This is confirmed in figure 3.5, which shows the standard deviation against the viscosity for 14 fluids tested, at the four shear rates: 7×10^4 , 1×10^5 , 2×10^5

and $3 * 10^5 \text{ s}^{-1}$. For each fluid and each shear rate, 30 repeats were performed. The standard deviation does not depend on the viscosity but decreases with increasing shear rate. The mean standard deviations for each shear rate over these 14 tests are listed in table 3.2. A relatively high number of repeats (at least 30) is needed to compensate for the large scattering. The large scattering at low shear rates is due to the design of the USV rig, which is less suited for this test. To obtain good repeatability, it is necessary to have a good alignment of the rotor in the stator. With a bigger gap between the rotor and the stator, and at low speeds (low shear rates), there is a higher chance that the rotor is misaligned and rotates with a slight angle. This generates low accuracy in the measured viscosity.

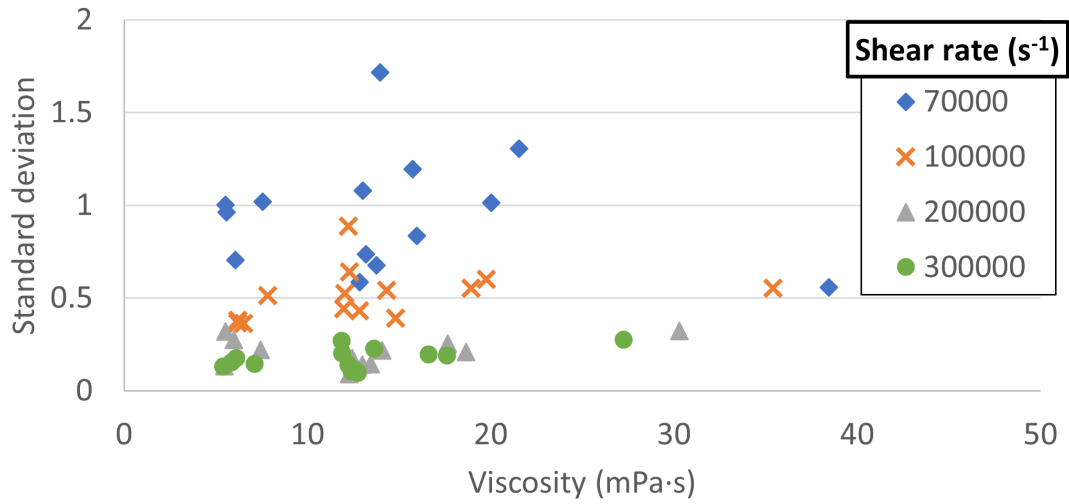


Figure 3.5: Standard deviation calculated over 30 repeats for 14 fluids tested at 4 shear rates

Table 3.2: Mean standard deviation over 14 tests for the four shear rates in the big gap configuration of the USV

Shear rate (s^{-1})	Mean standard deviation ($\text{mPa}\cdot\text{s}$)
70000	0.96
100000	0.51
200000	0.20
300000	0.17

3.4 Experimental rheology techniques to probe the properties of fluids in an EHD contact

The rheological and tribological responses of a fluid in the EHD regime can be measured using conventional techniques such as friction measurements [46], film thickness measurements [127, 124], high-pressure rheometry [128, 129] and high-shear rheometry [130, 131]. One limitation of conventional friction measurements is that a single value of the friction coefficient is acquired for the whole EHD contact. In an EHD ball-on-flat contact, the pressure, hence the viscosity and the friction, are heterogeneous in the contact. The distribution of pressure in the contact is commonly approximated as Hertzian. Performing single-value measurements does not give a full overview of the rheology in the contact and does not reflect the large variations of viscosity sustained by the fluid. Alternative techniques have to be used to perform local and *in situ* measurements in an EHD ball-on-flat contact.

3.4.1 Spectroscopy techniques applied to EHD contacts

Various techniques have been developed for the direct measurement of flow, local viscosity and pressure of thin fluid films in a confined environment. In situ techniques in an EHD tribological contact based on spectroscopy include (but are not limited to) those listed in table 3.3.

Table 3.3: Spectroscopy techniques developed for *in situ* observations of an EHD contact

Technique	Output	Reference
Infrared microreflexion absorption spectroscopy	Local pressure and molecule alignment	[88]
Infrared spectroscopy	Temperature rise distribution	[132]
	Molecule alignment and temperature distribution	[133]
Raman spectroscopy	Pressure distribution	[134, 135]
Fluorescence depolarisation	In situ viscosity	[136]
Particle tracking	Fluid flow profile	[137, 21]
Fluorescence spectroscopy	Fluid flow profile	[138]
Photobleached imaging	Fluid flow profile	[139]
Phosphorescence imaging	Fluid flow profile	[23]
Fluorescence lifetime	Viscosity map	[140]
Fluorescence anisotropy	Viscosity map	[141]

3.4.2 Luminescence time-resolved spectroscopy

Photo-luminescence has been proven to be suitable for local and *in situ* rheology measurements in an EHD contact. Photo-luminescence is the emission of light from a substance after excitation by photon absorption. Depending on the state of excitation, two different processes occur to allow the substance to return to the ground state: fluorescence and phosphorescence. Fluorescence is the rapid emission of a photon from an excited singlet state. The fluorescence lifetime (average time between excitation and return to ground state) of a fluorophore is typically 10 ns. Phosphorescence is a slower process, taking place when the excited state is a triplet excited state. Phosphorescence lifetimes are typically in the range of milliseconds to seconds. Common fluorescent fluorophores are quinine, rhodamine, pyridine, Nile red. The absorption and fluorescence emission spectra of Nile red is given in figure 3.6. The energy of the emission is lower than the energy of absorption, so the emitted photon has a longer wavelength than the absorbed photon. This phenomenon is called the Stokes shift.

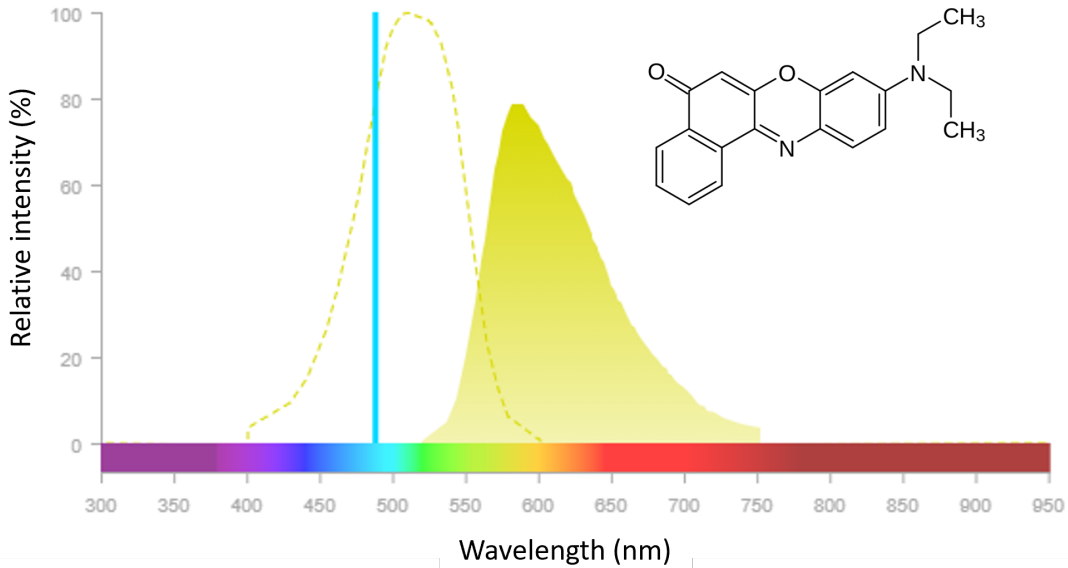


Figure 3.6: Absorption (dashed) and fluorescence emission (filled) spectra of Nile red. Excitation wavelength is 488 nm (blue). Generated using [142].

Time-resolved fluorescence is used to measure intensity decay. The fluorophores in solutions are excited by a short laser pulse and the intensity decay is recorded (nanosecond timescale). Intensity decays are typically mono-exponential, given by

$$I(t) = I_0 e^{-t/\tau} \quad (3.2)$$

where t is the time, I_0 is the intensity at $t = 0$, I the intensity at t , and τ the lifetime. For complex systems, the intensity decay can have a different form, for example

bi-exponential. The intensity decay gives information at the molecular level. It has been shown that the fluorescence lifetime of some fluorophores is directly related to the pressure or viscosity of their local surrounding environment [143, 144]. Dench *et al.* have successfully used this property of the fluorophore Thioflavin-T to map the viscosity of IGEPAL [140]. The authors' results evidenced the viscosity heterogeneity in an EHD contact. They restricted their work to hydrophilic systems due to limitations on the dyes that can be used with this technique.

Phosphorescence spectroscopy has also been used in EHD contacts to reconstruct velocity profiles. The technique relies on the long lifetime of the fluorophore to track the evolution of the phosphorescence intensity over time in a rolling-sliding EHD contact. Galmiche *et al.* [23] evidenced shear localisation of a polyphenyl ether using this technique. The central film thickness in their experiments was relatively high, ranging from 1 μm to 1.2 μm . If improved, this technique has the potential to unlock the investigation of complex flows in EHD contacts. The study of polymer solutions would benefit from the use of phosphorescence imaging velocimetry as little is known about their rheological response and velocity profiles in EHD contacts.

3.4.3 Fluorescence anisotropy

As stated in the previous section, Dench *et al.* could only work with hydrophilic systems with the fluorescence lifetime technique [140]. To address this issue and be able to work with oil-based systems, they developed another technique based on fluorescence anisotropy [141]. Utilising this technique, they successfully obtained viscosity maps of an EHD contact for PAO 8 at different pressures, up to a viscosity of 7.6 Pa.s. Fluorescence anisotropy is an optical method characterising the rotational diffusion of fluorophores. When excited by polarised light, fluorophore molecules with adsorption dipoles aligned with the incident light are preferentially excited. Due to rotational diffusion, these molecules rotate while they are in the excited state. Consequently, their emitted light is depolarised, as illustrated in figure 3.7. For a vertically polarised excitation light, the anisotropy r is quantified by the intensities of the vertically and horizontally polarised emissions, respectively $I_{\parallel}$ and $I_{\perp}$, equation 3.3. More details on fluorescence anisotropy can be found in [145].

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (3.3)$$

Anisotropy depends on intrinsic properties such as the size of the fluorophore but also on external factors such as viscosity. Fluorophores in very viscous solutions rotate more slowly during their excited state than when they are in less viscous solutions; i.e. anisotropy increases with viscosity. The relationship between anisotropy r and viscosity

η is given in equation 3.4,

$$r = A \ln \eta + B \quad (3.4)$$

where the two coefficients A and B depend on the chemistry of the species and on the dye. Therefore, A and B are not universal constants that can be found in the literature. A calibration is needed to determine them, only then viscosity can be derived quantitatively from anisotropy measurements.

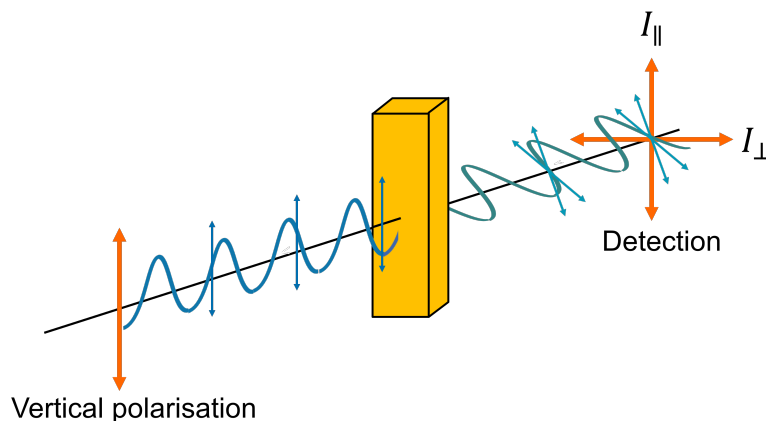


Figure 3.7: Fluorescence anisotropy: the incident light is polarised, the light emitted by the dye molecules is depolarised.

3.4.4 In situ Raman spectroscopy

Raman spectroscopy is a scattering technique which studies the vibrational modes of molecules. The excitation light, typically a laser, is scattered by the Raman active chemical bonds of the molecules. The scattered light can be categorised as Rayleigh scattering or Raman scattering. Rayleigh scattered light has the same wavelength as the laser so is eliminated with a notch filter or a longpass filter. Raman scattered light gives qualitative information - the wavenumber (or Raman shift) of each peak corresponds to a specific molecular bond vibration - and quantitative information - the intensity of the peak is proportional to concentration. The relative intensity of peaks can hence be used to estimate the relative concentrations of species in a mixture.

The Raman spectrum displays modes of vibration (stretching, bending) of the bonds that are Raman active. For example, a peak at 1650 cm^{-1} corresponds to a C=C bond stretching, a peak at 3600 cm^{-1} corresponds to a O-H bond stretching, and a peak at 1000 cm^{-1} corresponds to a angle bending between C and a H in $-\text{CH}_3$.

An example of a Raman spectrum is given in figure 3.8. The Raman scattered light comes directly from the fluid itself. Hence, Raman spectroscopy, unlike fluorescence or phosphorescence spectroscopies, has the advantage of not requiring any additional species such as dyes to be added to the fluid.

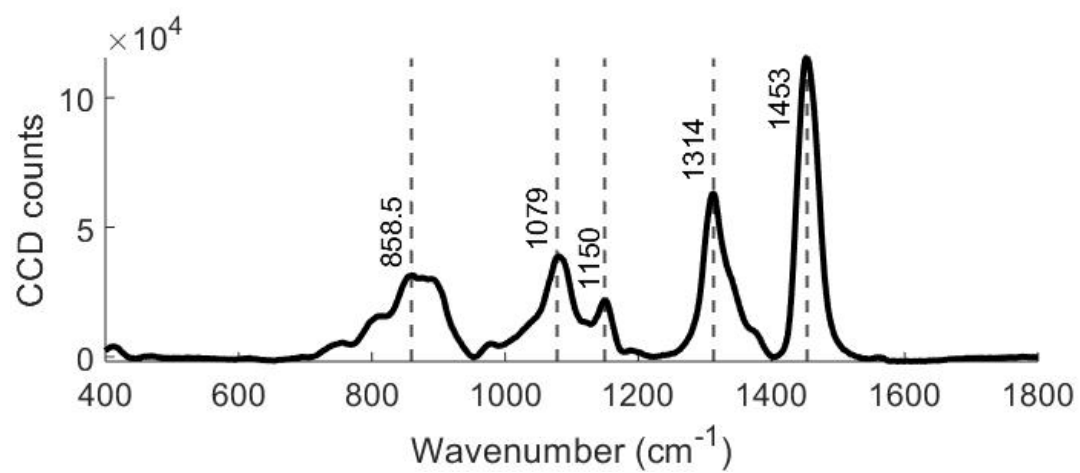


Figure 3.8: Raman spectrum of PAO 150

Chapter 4

Flow behaviour of polymer solutions in an elastohydrodynamic contact

In this chapter, velocity profiles of polymer solutions are investigated *in situ* in an EHD contact, using a phosphorescence imaging velocimetry technique. Velocity profiles of polymer solutions can deviate from a Couette flow because of slip or adsorption of the polymer on the contact surfaces, inducing a non-homogeneous shear behaviour in the fluid. The effect of solvent and of polymer molecular weight are studied. The case of copolymers is also explored.

4.1 Introduction

Reducing friction in engineering components is at the heart of tribology at this time, for instance to improve fuel economy in vehicles. Lubricants are a very effective tool to reduce friction, and their performance is enhanced using additives in their formulation, such as, to mention just a few, friction modifiers, anti-wear additives, antioxidants and viscosity modifiers [7].

Viscosity modifiers are polymeric additives which primary function is to increase the viscosity of lubricants. They improve the viscosity-temperature relationship while ensuring a good shear stability of the oil. They are widely used in engine lubricants, automatic transmission fluids, power steering fluids, industrial gear oils, and aircraft piston engine oils [7]. For details on viscosity modifier additives functions, chemistries and mechanisms, the reader is referred to the review by Martini *et al.* [69].

In the elastohydrodynamic regime, the shear-thinning mechanism has been linked to the friction reduction observed with viscosity modifier-containing lubricants [94]. Shear-thinning can be detrimental in some applications as it causes a lower film thickness and viscosity, however, a lower friction is favourable for fuel economy. The shear dependance of polymer solutions was introduced in section 2.7.

Another well-known way of reducing friction is through slip of the liquid at the contact surfaces. Boundary slip and its effect on film thickness and friction was introduced in section 2.2.1 and in section 2.9.3. Choo *et al.* [146] developed a low load tribometer and concluded from experiments conducted using n hexadecane and different contact surfaces that the lower friction results were most likely linked to slip. Fillot *et al.* [147] proposed an improved numerical model including nanoscale slip for the modelling of EHD lubrication, and obtained lower friction compared to the classical friction prediction that assumes no slip. Friction reduces when slip occurs as slipping surfaces cannot transfer as much momentum to the fluid as in the no-slip case, thus the shear stress is lower [26, 148].

This chapter aims at answering the following questions:

- *Does the flow behaviour of polymer solutions and copolymer solutions deviate from a Couette flow?*
- *What are the possible mechanisms responsible for the deviations?*

In this work, the presence of slip for viscosity modifier-containing lubricants in a tribological contact in the elastohydrodynamic lubrication regime is investigated. Polymer systems are good candidates to study slip at solid-liquid interfaces as previous research showed that confined polymer solutions exhibit slip under certain conditions [119, 149, 150]. Many experimental techniques have been developed to observe slip, including particle image velocimetry [151, 152], photobleached-fluorescence imaging velocimetry [116], particle tracking velocimetry [153] and marker lines [154]. In this study, a phosphorescence imaging velocimetry technique was used. This *in situ* and real time technique allows access to the through-film velocity profiles of tribological contacts [23]. Interfacial slip is characterised by a discontinuity between the fluid velocity and the surface velocity at the surface. Therefore, this phenomenon can be detected in flow profiles [116].

The phosphorescence imaging velocimetry was used to study the velocity profiles of copolymers. Copolymers have gained recently a great interest for their potential use as dual additives. Viscosity modifiers seem to be good candidates to also play the role of friction modifiers [155]. Polymeric additives adsorbing on the contact surfaces form a boundary film that leads to a reduction in friction [79]. Recent studies in the boundary lubrication regime have confirmed that functionalised copolymers have the potential to be friction modifiers in addition to their use as viscosity modifiers [79, 156, 82].

4.2 Methodology

4.2.1 Phosphorescence spectroscopy

In this work, phosphorescence spectroscopy is used to reconstruct velocity profiles in a tribological contact. A fluorophore, such as a dye, reaches its excited state when exposed to light. It then returns to its ground state of energy by emission of a photon, through two phenomena: fluorescence or phosphorescence. Fluorescence has a lifetime in the order of 10 ns, while phosphorescence is a much slower process with a lifetime ranging from milliseconds to seconds. Principles of fluorescence and phosphorescence were discussed in section 3.4, and the reader can refer to the book by Lakowicz [157] for more details on luminescence. For both fluorescence and phosphorescence, the energy of the emission is lower than the energy absorbed (Stokes shift). This means that the emitted photon has a longer wavelength than the excitation source, which allows a discrimination of the excitation light and the emitted light by using filters, such as bandpass or notch filters. It is hence possible to collect the intensity from the fluorophore and develop phosphorescence spectroscopy techniques. The response of the fluorophore can provide insightful information on its local environment in a wide range of applications, for example to detect DNA in analytical biochemistry [158], to perform temperature measurements *in situ* in the piston of a thermal engine [159], or to study the rheology of thin films [19]. Phosphorescence imaging velocimetry has proven to be an effective method to access through-thickness velocity profiles of lubricants in a tribological contact [23]. Galmiche [23] used this technique to reconstruct velocity profiles of a polyphenyl ester in a tribological contact and successfully studied the effect of contact pressure on the flow of the lubricant. They observed a Couette flow at low pressure and more pronounced shear banding as they increased the pressure [23]. The central film thickness with this polyphenyl ester was ranging between $1\ \mu\text{m}$ and $1.2\ \mu\text{m}$ [23]. In this chapter, the phosphorescence spectroscopy technique is used to access the velocity profile of polymer solutions. Improvements are made, and a new methodology for the background correction is proposed, so that polymer solutions with a central film thickness as low as $80\ \text{nm}$ can be studied.

4.2.2 Phosphorescence imaging velocimetry

Phosphorescence imaging velocimetry was used to access velocity profiles in a tribological contact in the elastohydrodynamic regime. The experimental setup is shown in figure 4.1. It consisted of a tribological ball-on disc contact with a microscope built on top of it. The experimental platform, an EHD1 by PCS instruments (Acton, UK), was used to carry out the experiments in the elastohydrodynamic regime, where the two contact

surfaces elastically deform and are fully separated by a thin film of lubricant. The ball was immersed in the lubricant and loaded against the disc. The entrainment speed and slide-to-roll ratio were controlled, as well as the temperature of the lubricant and the load. Both ball and disc were glass specimens. They were cleaned in toluene and sonicated for 30 minutes before each test. The EHD1 rig was cleaned with toluene.

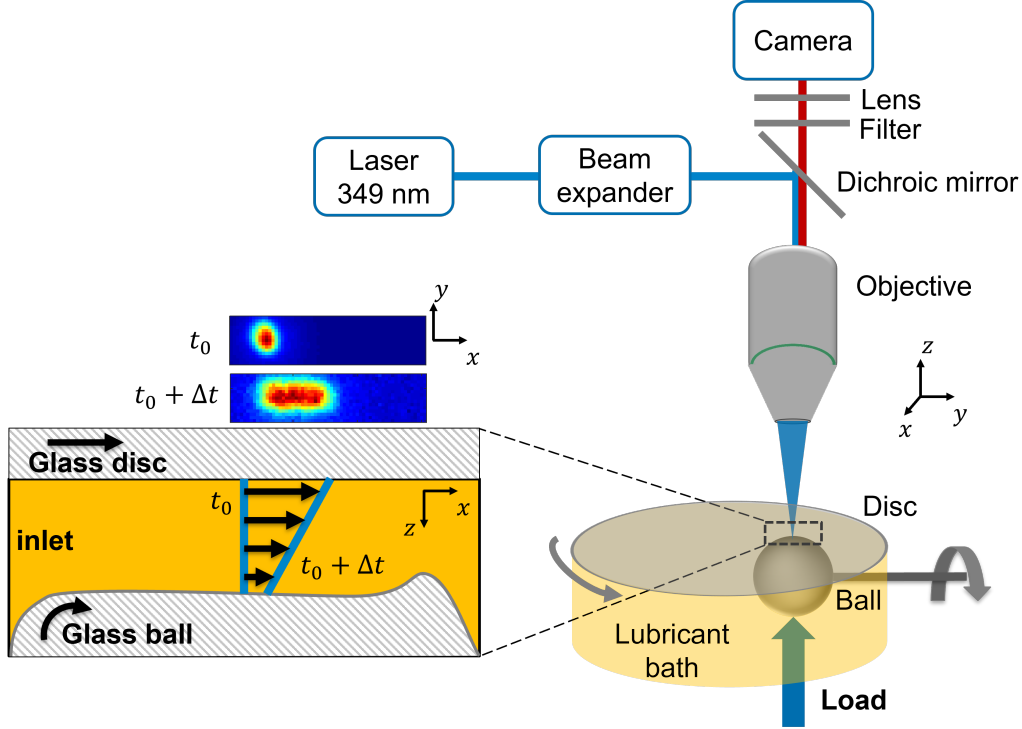


Figure 4.1: Schematic of the phosphorescence spectroscopy setup, with a zoomed-in representation of the ball-on-disc contact in the elastohydrodynamic regime on the left-hand side, in which the blue lines represent the initial column of excited dye molecules after the laser pulse at t_0 and how they would spread after a short time Δt in the case of a Couette flow. An example of phosphorescence images is shown above the contact.

The solutions were doped at a concentration of 2 mM with a dye, Tris(dibenzoylmethane) mono(1,10-phenanthroline)europium(III) from Sigma Aldrich. Its chemistry is shown in figure 4.2a. This dye will be referred to as Eu(DBM)3(Phen) in this thesis. Its lifetime depends on the fluid used, and on the conditions. See figure 4.2b for two examples, the lifetime τ of the dye is $58 \mu s$ to $133 \mu s$ in a copolymer solution and in DOP.

The doped lubricants (more information on the lubricants in section 4.3) were excited with a short laser pulse (< 5 ns) from a 349 nm laser (Spectra-Physics Explorer 349 nm) via a 20x objective (manufacturer: Olympus, numerical aperture: 0.5, depth of field: $1.10 \mu m$). The phosphorescence response was collected using the same objective and an intensified EMCCD camera (Hamamatsu Orca-R2). The spatial resolution was $0.99 \mu m/\text{pixel}$. The images were captured with an exposure time of $5 \mu s$.

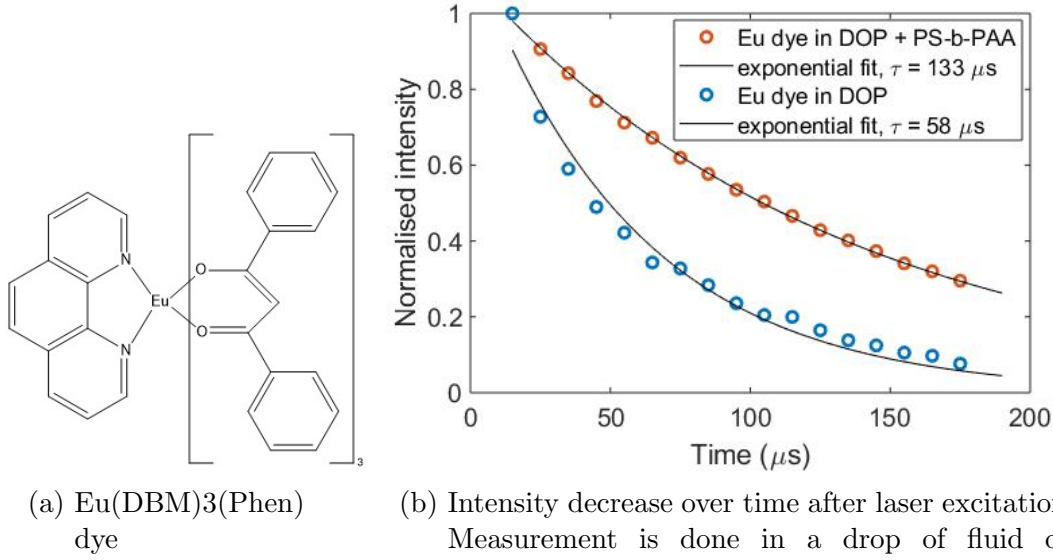


Figure 4.2: Chemical structure of Eu(DBM)3(Phen) and its phosphorescence lifetime in DOP and DOP + copolymer

A hall sensor on the disc was used to trigger the laser so that the laser pulse was always hitting the contact in the same position for each rotation of the disc. This created a spot where the intensity of the light emitted by the excited dye was then captured over time with the camera. At each position, five images were acquired and averaged in order to reduce noise. From these images, the phosphorescence response was known as a function of time and position. The first image was taken $2 \mu\text{s}$ after the laser pulse to ensure that only phosphorescence, and not fluorescence, was captured. The first phosphorescence image was captured $15 \mu\text{s}$ after the laser pulse, and subsequent images were taken at intervals of $10 \mu\text{s}$ or $20 \mu\text{s}$. The laser power was kept to the minimum value giving enough phosphorescence response. The fluorescence and phosphorescence from the contact surfaces increase with laser power, affecting the results, so the power was kept as low as possible to minimise this effect. A background correction was performed, and will be explained in details in section 4.2.4.

The through-film velocity profiles were reconstructed from the intensity distributions over time [23]. The reconstructive scheme assumes the flow to be governed by advection. The film is modelled through the thickness as 30 layers of fluids that all move independently. The relationship between the phosphorescence intensity and the velocity distribution is solved numerically by comparing theoretical intensity distributions to the experimental intensity distribution, using a non-linear least squares regression.

The first phosphorescence image captured is used to check the shape of the

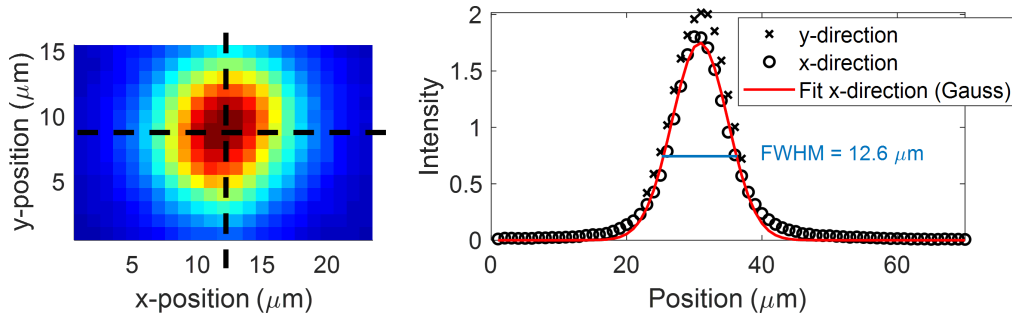
phosphorescence response in the x-y plane. The phosphorescence spot should be circular. The fit of the intensity of the phosphorescence spot is either Gaussian or Lorentzian, depending on the experiment performed. It is unclear why the shape was not consistent through experiments. A Gaussian distribution is given by

$$I(x) = I_0 \frac{-(x - x_c)^2}{2w_0^2} \quad (4.1)$$

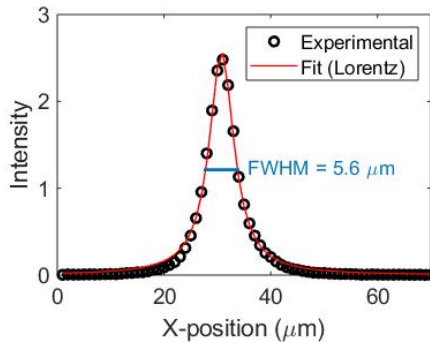
where I is the intensity, I_0 is the peak intensity at the centre x_c of the distribution, and w_0 is the phosphorescence response radius where the intensity has decreased to $1/e^2$. A Lorentz distribution is given by

$$I(x) = \sqrt{\frac{\pi}{2}} \frac{ac^2}{4(x - x_c)^2 + c^2} \quad (4.2)$$

where I is the intensity, $\sqrt{\pi/2}a$ is the peak intensity at the centre x_c of the distribution, and c is the FWHM (full width half minimum) of the Lorentzian distribution.



(a) DOP in the ball-on-disc contact in pure rolling, $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C. Left is image of first spot after laser excitation. Right is intensity in x- and y-directions following dotted lines (average over 5 pixels), with Gaussian fit for x-direction.



(b) DOP + 0.05 wt% PS-b-PAA 197.0-b-190 kDa, drop on a glass slide under the microscope (static conditions). Lorentzian fit.

Figure 4.3: Intensity distributions of the phosphorescence response after laser excitation.

Figure 4.3 shows two examples of intensity distributions of phosphorescence spots, for DOP in the contact under pure rolling conditions and for a copolymer solution under static conditions (drop of fluid on glass slide). In all experiments, the FWHM of the intensity distribution of the phosphorescence response is between 5 and 13 μm . The FWHM was different from an experiment to another, depending on the laser power, the quality of the alignment and of the focus.

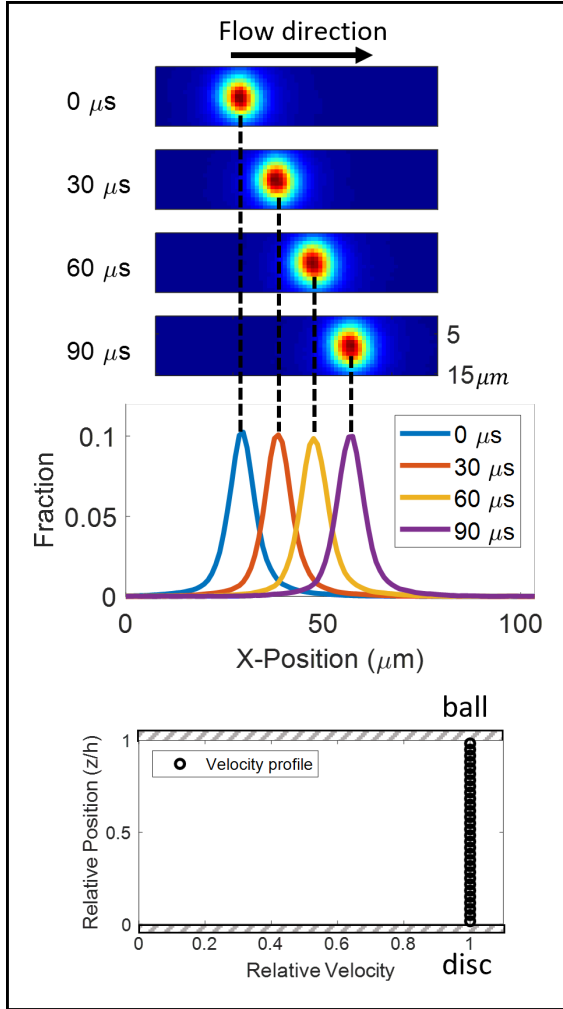
To illustrate the flow of lubricants under a no-slip boundary condition, figure 4.4 shows two examples of through-thickness velocity profiles $u(z)$, along with the phosphorescence images and corresponding normalised intensity distributions, obtained in pure rolling and pure sliding conditions, respectively for a polymer solution and a polyphenyl ether, 5P4E. Each phosphorescence image is normalised individually with its total intensity, as the intensity decreases exponentially with time due to the lifetime of the dye. The relative velocity is defined as

$$relative\ velocity = \frac{u(z/h) - U_e}{\Delta U} \quad (4.3)$$

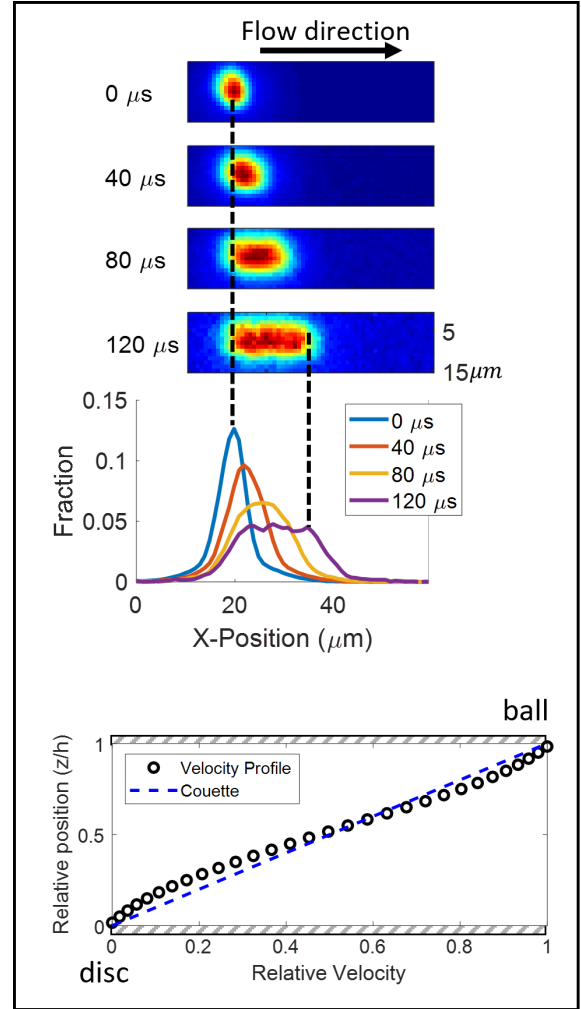
where z is the position along the vertical z -axis, h the film thickness, U_e the entrainment speed and ΔU the sliding speed. In pure rolling, the two surfaces have the same speed and both have a relative velocity of 1. At other SRRs, the relative speed of the slow surface is 0 and the relative speed of the fast surface is 1. The relative position z/h is the position through the thickness, with the disc at $z = 0$ and the ball at $z = 1$

In figure 4.4a, note that the shape of the excited spot does not change, all the molecules in the through-film column excited by the laser pulse travel at the same speed. The velocity of the fluid is the same as the velocity of the two contact surfaces (relative velocity of 1 throughout the thickness of the film), which means that the system is not experiencing interfacial slip. A fluid under pure rolling conditions that obeys the no-slip boundary condition does not experience any shearing.

When shearing 5P4E under pure sliding conditions (figure 4.4b), the spot on the first phosphorescence image is circular, and then stretches as the fluid is sheared, as seen on the subsequent images. The intensity of the stretched spot is relatively uniform along the flow direction. This is characteristic of a Couette flow, i.e. velocities vary linearly between the two contact surfaces. This is consistent with the literature which showed that 5P4E has a near-Couette flow profile under these conditions [23]. Since there is no slip, the velocity of the liquid at the proximity of the walls is the same as the speed of the walls.



(a) DOP + 4.8 wt% PS ($M_w=192$ kDa),
pure rolling,
 $P_{max}=271$ MPa, $U_e=0.3$ m/s, $T=14$ °C.

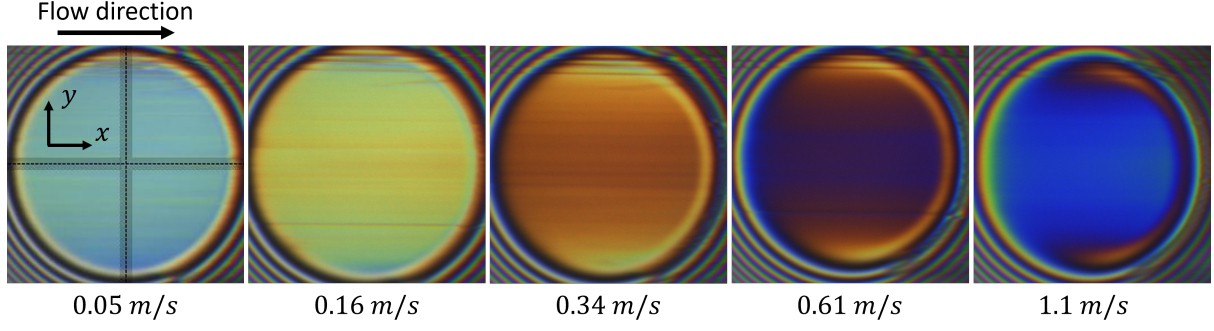


(b) 5P4E,
pure sliding (ball faster),
 $P_{max}=188$ MPa, $U_e=0.072$ m/s, $T=25$ °C.

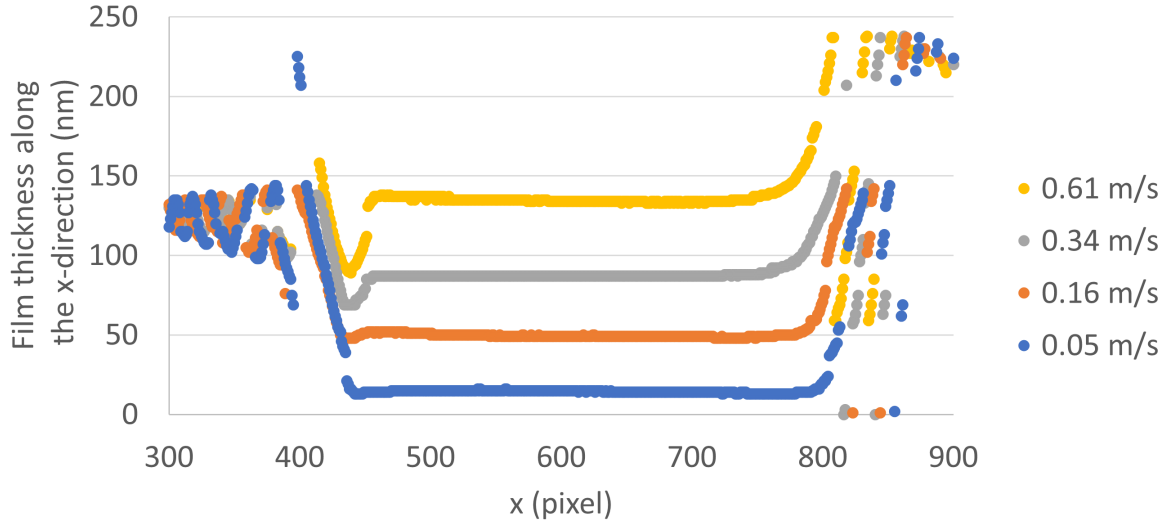
Figure 4.4: Phosphorescence images, normalised intensities and velocity profiles. The first image is taken as the time reference. The dashed line in the velocity profile corresponds to a Couette flow.

4.2.3 Homogeneity of the film thickness in the contact

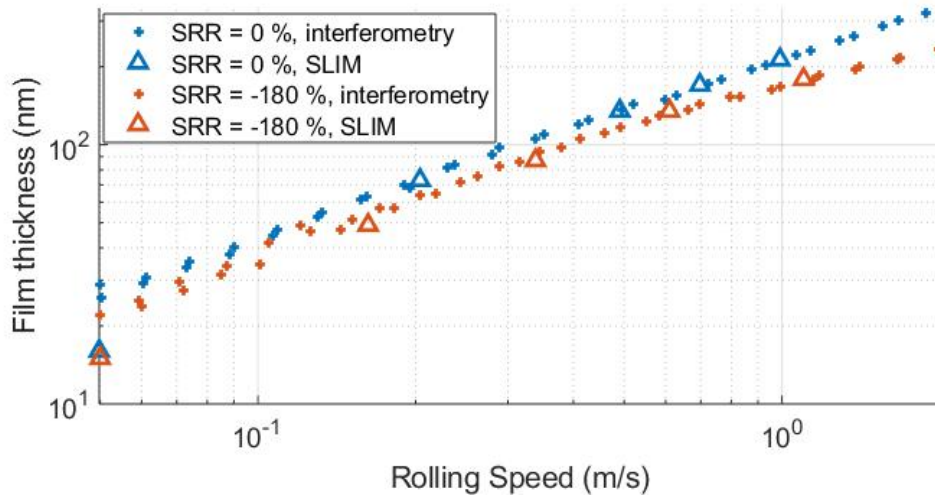
In this phosphorescence spectroscopy technique, the excited dye molecules travel between 30 and 60 μm in the contact during the acquisition of the images, depending on the entrainment speed and SRR . To verify the uniformity of the film thickness along the contact, SLIM experiments using an EHD2 rig by PCS Instruments were conducted. With SLIM (spacer layer imaging method), maps of the film thickness in the contact are obtained [127]. The specimens used for SLIM are a steel ball and a glass disc coated with a chromium layer and a silica layer. A glass ball could not be used as this technique requires the ball to be reflective. The SLIM images for DBP + 8 wt% PS 35 kDa, with their corresponding film thickness across the centreline of the contact, in the direction of the flow, are given in figure 4.5 (figures 4.5a and 4.5b). Finally, figure 4.5c compares the central film thickness measured in the centre of the SLIM images to the film thickness measured with the optical interferometry technique. Figures 4.5a and 4.5b confirm that the film thickness is homogeneous in the direction of the flow in a large region of the contact. This observation is valuable for the use of an optical velocimetry technique, as it means the approximation that the two surfaces are two parallel plates is valid, i.e. no wedge effect has to be considered in the contact. It can be observed in figure 4.5c that there is a good agreement in the film thicknesses obtained using the two different techniques, SLIM and optical interferometry. Only a deviation in film thickness between the two techniques is observed at the lowest speed 0.05 m/s. This speed is out of the range of speeds used in this study, the cause of the deviation was not investigated. The film thickness is slightly lower at high SRR , presumably due to shear thinning and shear heating of the fluid. Note that these SLIM and film thickness results are obtained under higher pressures than the pressures used in the phosphorescence imaging velocimetry technique.



(a) SLIM images at different rolling speeds, for $\text{SRR} = -180\%$, $T=25\text{ }^{\circ}\text{C}$ and $P_{\max} = 526\text{ MPa}$



(b) Film thickness from the SLIM images for $\text{SRR} = -180\%$, along the x-direction as represented in the first image of subfigure (a). $T=25\text{ }^{\circ}\text{C}$ and $P_{\max} = 526\text{ MPa}$.



(c) Comparison between the central film thickness using interferometry and using SLIM for $\text{SRR} = 0\%$ and $\text{SRR} = -180\%$ (ball faster).

Figure 4.5: SLIM images and film thickness for DBP + 8 wt% PS 35 kDa, at $T=25\text{ }^{\circ}\text{C}$ and $P_{\max} = 526\text{ MPa}$, steel ball against glass disc contact.

4.2.4 Background correction

One of the main challenges in this phosphorescence imaging velocimetry experiment was the intensity of the dye phosphorescence. The fluids used in this work were less viscous than the fluids used in previous studies (polybutene [139] and 5P4E [23]). More details on the fluids will be found in the next section 4.3. Despite using a higher rolling speed to increase the film thickness, the latter was relatively small, smaller than 300 nm. As a thinner film gives a lower phosphorescence intensity (fewer dye molecules are hit by the laser beam), not only the signal-to-noise ratio was low, but the phosphorescence from the contact surfaces was relatively stronger. This had to be addressed by performing a robust background correction that eliminates the phosphorescence originating from the contact surfaces. An effective way of collecting the phosphorescence from the contact surfaces only is to run the experiment under the exact same conditions but with a fluid that does not contain the dye. However, this is challenging in practice as without dye in the solution, the contact cannot be seen and finding the right focus in the contact becomes very difficult. To overcome this problem, the test without dye was done straight after the test with dye, so the focus and contact position did not have to be adjusted. The fluid with dye was poured out and replaced by the fluid with no dye, but the contact surfaces were not changed to ensure that the contact would stay at the same position. To perform the background correction, the intensity from the images acquired with no dye was subtracted to the raw intensity of the images acquired with dye.

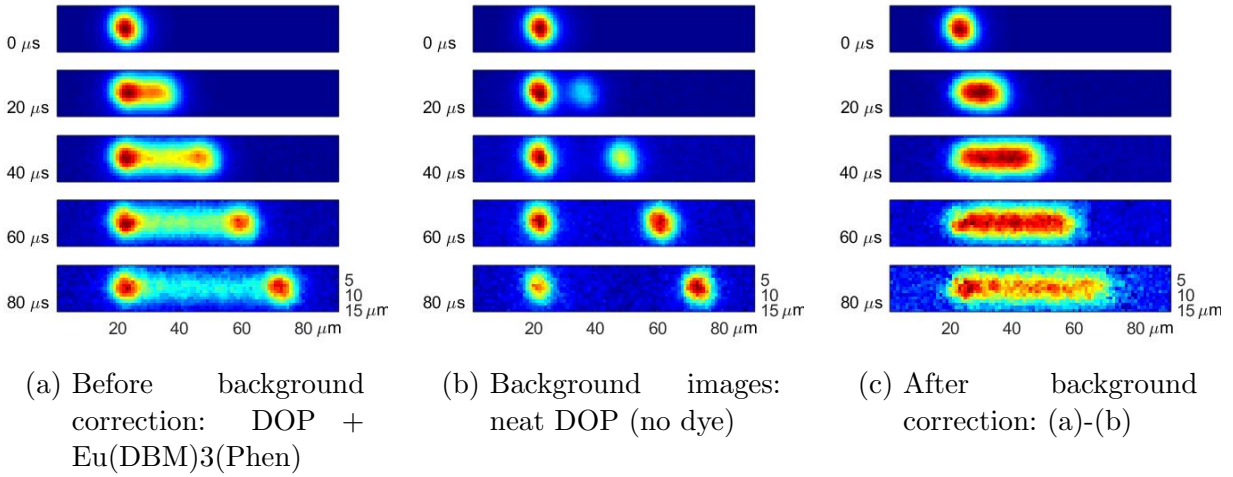
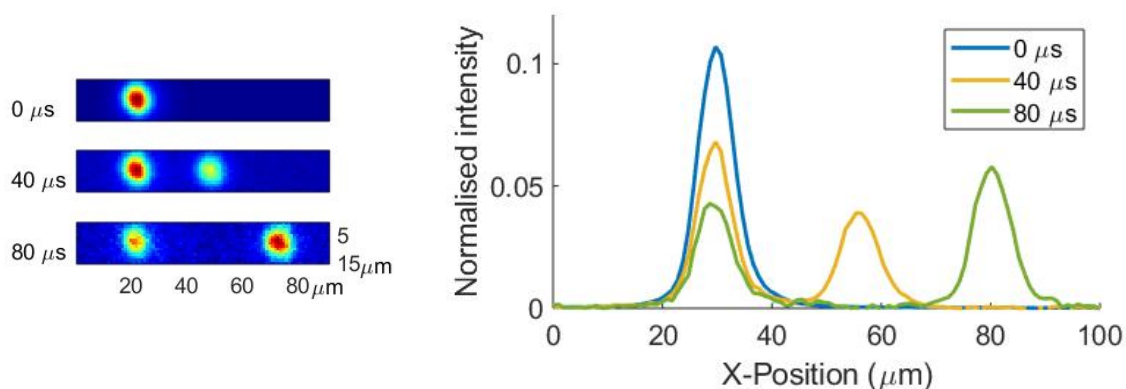


Figure 4.6: Intensity over time for DOP, $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C. First image is taken as time reference. Flow direction is left to right on each set of pictures

An example of background correction is shown in figure 4.6 for a phthalate ester, dioctyl phthalate (DOP), at 25 °C and under pure sliding conditions (disc is stationary, ball rotates). Under these conditions, the central film thickness is estimated to be 138 nm. The film thickness was measured by optical interferometry at a SRR of -180 %, and due to the limitations of the EHD2 rig, a SRR of -200 % could not be achieved. The measurement at -180 % gives a good estimation of the film thickness as for DOP, only a small decrease of film thickness was observed with an increase of SRR. Note that in figure 4.6, the intensity is normalised independently for each picture. The phosphorescence intensity decreases exponentially with time, hence the raw intensity at $t = 80 \mu s$ is much lower than at $t = 0 \mu s$. The pattern at $t = 80 \mu s$ would be barely visible without normalisation. The strong phosphorescence from the contact surfaces can be seen in figure 4.6b, which is the case with no dye in the fluid. There are two distinct bright spots, one stationary over time from the disc, and one moving from the ball. After subtraction of the background on the raw intensity, figure 4.6c, the intensity appears more homogeneous through the direction of the flow, which is consistent with the fact that a Couette flow is expected in this case.

To check that only the phosphorescence of the contact surfaces is collected during the acquisition of the background images, the intensity along the x-direction (direction of the flow) across the centreline of the contact is plotted. Figure 4.7 shows three of the phosphorescence images for DOP (same conditions and images as in figure 4.6b) along with the corresponding normalised intensities. In the space between the position of the disc (left spot) and the position of the ball (right spot), the intensity is zero. This confirms that during the background correction procedure, no signal is collected from the fluid and that the phosphorescence is only due to the contact surfaces.



(a) Background phosphorescence images, neat DOP (no dye).

(b) Corresponding normalised intensity at the centreline ($y = 10 \mu m$) in the direction of flow.

Figure 4.7: Background phosphorescence images for DOP, $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C. First image is taken as time reference. Flow direction is left to right.

4.3 Polymer solutions

4.3.1 Choice of the solvent

For the selection of the solvents, the constraints were:

- the dye $\text{Eu}(\text{DBM})_3(\text{Phen})$ must dissolve in the fluid and have a long enough phosphorescence lifetime and intensity to perform the experiments
- the polymer must dissolve in the fluid
- the fluid must have a relatively high viscosity to ensure a film thick enough to give a high phosphorescence intensity after excitation

PAO lubricants are commonly used in tribological studies, but $\text{Eu}(\text{DBM})_3(\text{Phen})$ does not dissolve in them as this dye is polar and PAO oils are apolar. Consequently, esters were considered, as they are available in different viscosities, are widely used and cheap. Esters are also efficient lubricants for electric vehicles and have the advantage of having a low toxicity and being bio-sourced (see section 2.3). Trioctyl trimellitate (TOTM) was a potential candidate, as well as Dibutyl phthalate (DBP) and Dioctyl phthalate (DOP). Their chemical structures can be found in figure 4.8, and their properties are listed in table 4.1. These three esters were purchased from Sigma-Aldrich and used as received. The dynamic viscosity was measured with a Stabinger viscometer (Anton Paar) and the film thickness with an EHD2 (PCS Instruments).

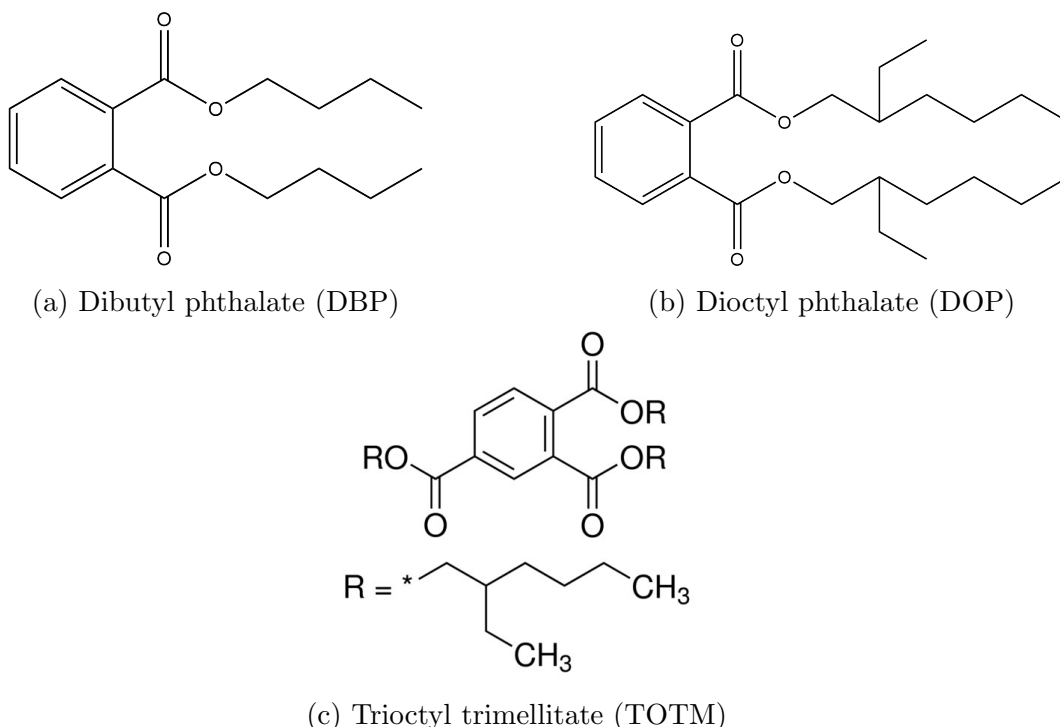


Figure 4.8: Chemical structure of esters used

Table 4.1: Viscosity and film thickness of the esters

Fluid	Dynamic viscosity η (mPa·s)			Central film thickness (nm)
	25 °C	40 °C	100 °C	T=25 °C, $U_e = 0.3$ m/s, $P_{max} = 526$ MPa, $SRR = 0$ %
TOTM	209.3	85.7	8.9	394.7
DBP	16.2	9.3	2.2	54.2
DOP	57.6	26.2	3.9	150

4.3.2 Choice of the polymers

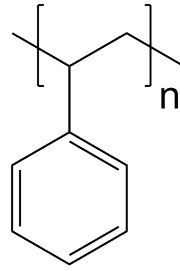
Concerning the choice of polymers, different chemistries and molecular weights were tested. They are listed in table 4.2. Unfortunately, none of these polymers could dissolve in TOTM (gentle stirring at 60 °C overnight). Only the two PS (in bold in table 4.2) could be dissolved in the phthalate esters DBP and DOP. It was decided to use TOTM without polymeric additive to study this fluid and gain confidence in the technique, as its high viscosity makes it easier to obtain flow profiles than with DOP and DBP. The polymer solutions are DBP+PS and DOP+PS, at concentrations ranging from 0.1 wt% to 5 wt% for DOP and up to 10 wt% for DBP. Two molecular weights were selected for PS: $M_w = 35$ kDa and $M_w = 192$ kDa (from Sigma-Aldrich). It can be noted in figure 4.8 that the two solvents DBP and DOP have close chemistries, DOP has slightly longer chains hence a higher viscosity. The chemistry of PS can be seen in figure 4.9.

Advantages of using PS are its low dispersity (close to the unity), its commercial availability for a wide range of molecular weights, and the fact that it has been extensively studied [160, 126]. Systems with PS in phthalate esters are common systems found in the literature, their viscometry was studied [161] as well as their behaviour under shear. Kume *et al.* [162] showed that when a solution of a high-molecular weight PS in DOP is under shear, PS molecules align with the flow. Marx *et al.* [93] found that under severe shear conditions ($10^6 - 10^7$ s⁻¹), PS molecules ($M_w : 50 - 200$ kDa) in phthalate esters undergo permanent shear thinning and degrade, leading to a drop of the solution viscosity. Previous works on phthalate esters and polystyrene suggest that these systems are good candidates to observe slip. Grzelka *et al.* [163] studied the slip behaviour and interfacial friction of PS in diethyl phthalate (DEP). They sheared a drop of the polymer solution between two substrates and measured the slip length using a photobleaching technique. Note that the shear rate experienced by the fluid in their work was relatively low, below 1 s⁻¹. In our study, we propose to investigate the flow behaviour at much higher shear rates, in the range of 10^4 - 10^7 s⁻¹, which are commonly encountered by lubricants.

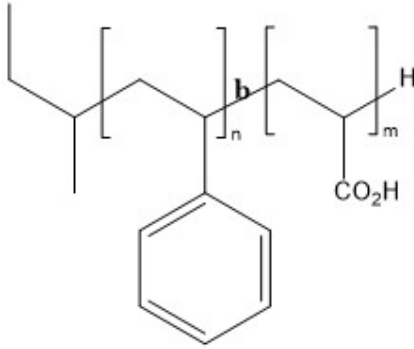
Two copolymers were also selected. Recent studies have highlighted the potential use of copolymers as dual additives, such as viscosity modifiers and friction modifiers [81, 82].

Table 4.2: Polymers considered for this study

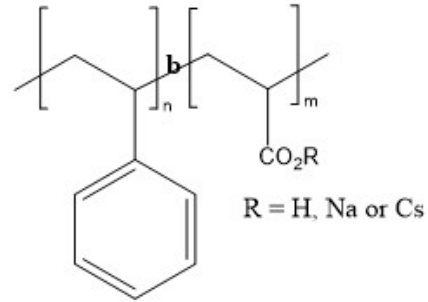
Polymer	Supplier	Molecular weight	Soluble in esters?
Poly(methyl methacrylate) (PMMA)	Sigma-Aldrich	$M_w = 15 \text{ kDa}$	No
Poly(methyl methacrylate) (PMMA)	Sigma-Aldrich	$M_w = 350 \text{ kDa}$	No
Poly(methyl acrylate) (PMA) solution	Sigma-Aldrich	$M_w = 40 \text{ kDa}$	No
Polybutene Indopol H-300 (PB)	Ineos Oligomers	$M_n = 1300 \text{ Da}$	No
Polybutene (PB)	Sigma-Aldrich	$M_n = 2300 \text{ Da}$	No
Polystyrene (PS)	Sigma-Aldrich	$M_w = 35 \text{ kDa}$	Yes
Polystyrene (PS)	Sigma-Aldrich	$M_w = 192 \text{ kDa}$	Yes



(a) Polystyrene



(b) PS-b-PAA, 41.0-b-4.2 kDa



(c) PS-b-PAA, 197.0-b-190.0 kDa

Figure 4.9: Chemical structure of polymers used

Block copolymers have one block adsorbing on the contact surfaces, which could change the behaviour of the liquid at the interfaces. They can also form micelles, which may then aggregate at the inlet due to their big size. Both phenomena could potentially impact the film thickness and velocity profile in the contact. For these reasons, they are of particular interest in this study. As the solvents DBP and DOP, and dye Eu(DBM)₃(Phen) remain unchanged, it was decided to use Poly(styrene-*b*-acrylic acid) block copolymers, referred also as PS-*b*-PAA in this thesis. The phthalate esters DBP and DOP are good solvents for the PS block, while being bad solvent for the PAA block, the latter is hence likely to aggregate and form micelles. Two PS-*b*-PAA copolymers were purchased from Polymer Source, their properties are listed in table 4.3.

Table 4.3: Copolymers PS-b-PAA and their properties

Polymer	Supplier	Molecular weight $M_n * 10^3$	Polydispersity index
PS-b-PAA	Polymer Source	41.0-b-4.2	1.08
PS-b-PAA	Polymer Source	197.0-b-190	1.10

4.3.3 Preparation of the polymer solutions

PS was dissolved in DOP and DBP by magnetic stirring for 2 days at 60 °C. The final solutions are 9.9 wt% PS in DBP and 4.8 wt% PS in DOP.

The copolymers PS-b-PAA were more difficult to dissolve. PS-b-PAA 41.0-b-4.2 kDa was dissolved in DOP by magnetic stirring for 2 days at 80 °C then 2 days at 100 °C. The final solutions are 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa in DOP and 0.5 wt% PS-b-PAA 197-b-190 kDa in DOP. The long copolymer PS-b-PAA 197-b-190 kDa could not be dissolved at a concentration of 0.5 wt% in DOP, even after two weeks of stirring at 150 °C. The solution was then diluted and the final copolymer concentration is estimated around 0.05 wt% (estimation as some bits of solid copolymer could not be dissolved so were filtered out). The copolymer solutions used in this work were prepared by Amran Mohamed (Tribology group, Imperial College London). The dye Eu(DBM)3(Phen) was dissolved last in all solutions by magnetic stirring for twelve hours at 60 °C.

4.3.4 Characterisation of the size of polymer molecules by dynamic light scattering

The size of the polymer molecules in solution was measured at 25 °C by dynamic light scattering (DLS) using a Zetasizer Pro from Malvern Panalytical. With PS, solutions of concentrations between 0.1 wt% and 10 wt% in DBP and between 0.1 wt% and 5 wt% in DOP were prepared and tested. The distributions of the size of PS are reported in figure 4.10. The diameter of PS 35 kDa molecules ranges between 14 and 32 nm in DBP and between 18 and 32 nm in DOP. The diameter of PS 192 kDa molecules ranges between 24 and 28 nm in DBP and between 24 and 50 nm in DOP. A first observation is that surprisingly, PS 192 kDa does not exhibit a bigger size in DBP than PS 35 kDa while having a higher molecular weight. The literature shows that in the dilute regime, the hydrodynamic radius of linear polymer molecules is a function of the polymer molecular weight (power law) [164, 165]. Hence, PS 192 kDa should have a higher diameter than PS 35 kDa. Tsunashima [166] measured the gyration radius of polystyrene 192 kDa in benzene (good solvent) in the dilute regime and found $R_g^2 = 2.5 * 10^{-12} cm^2$. This would give a diameter of 32 nm, a value very close to the one found for PS 192 kDa in DBP and

DOP. In figure 4.10b, a small increase in intensity is observed around 500 nm for the two highest concentrations (3.2 and 10 wt% in DBP), suggesting an aggregation of polymers. In figure 4.10, for each of the four graphs, the inserts give the diameter at the maximum intensity as a function of the polymer concentration. The trends have to be considered with care as the repeatability of the DLS measurement is poor. In figure 4.10d, it is unlikely that the size of PS in DOP increases with increasing concentration.

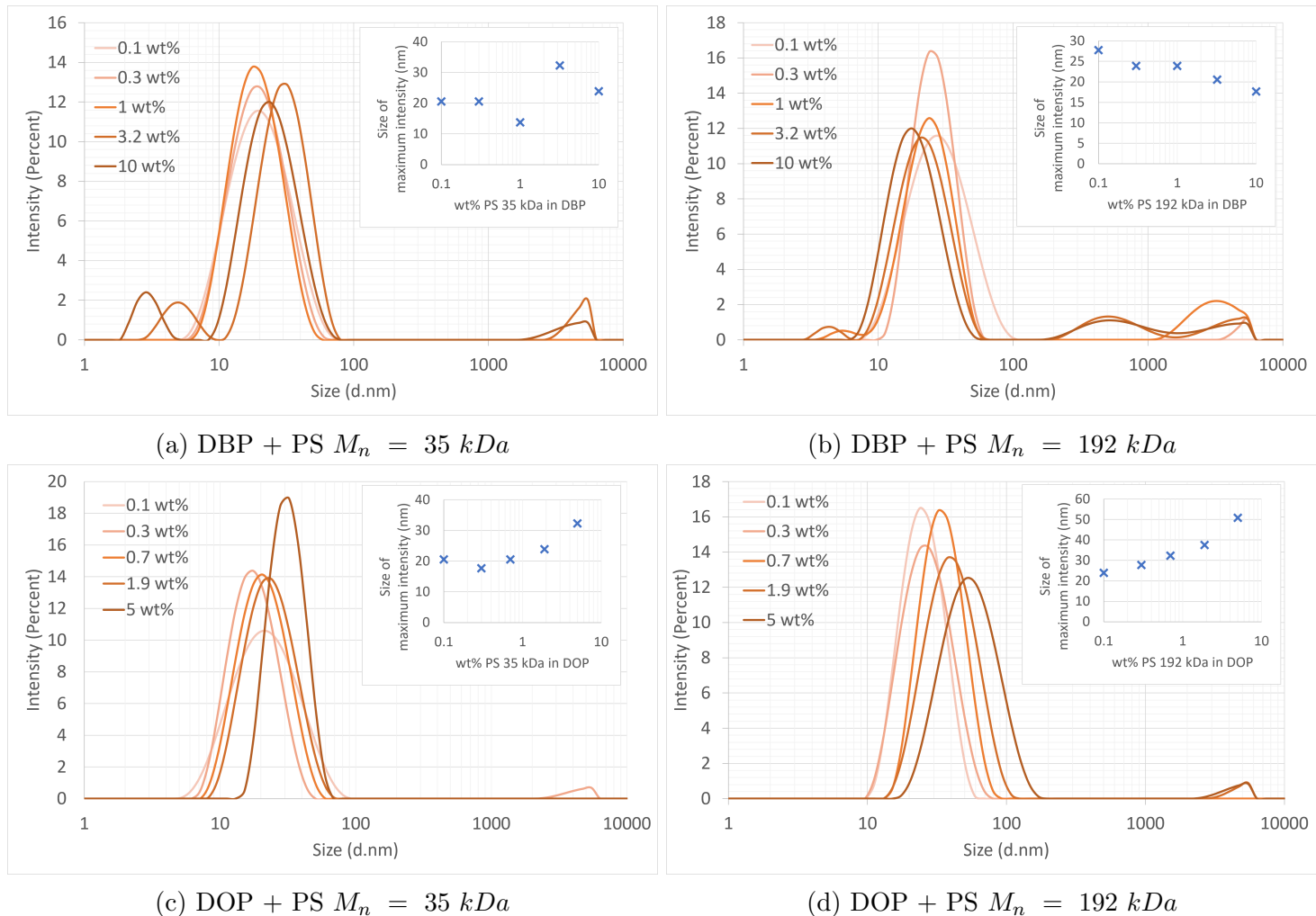


Figure 4.10: Distributions of the size of PS molecules in DBP and DOP at different concentrations at 25 °C. Inserts show the size of maximum intensity in the distribution against PS concentration.

The diameter of the two copolymers was measured in DBP. The preparation of the solutions and acquisition of the DLS data were performed by Amran Mohamed. Figure 4.11 shows that the diameter of the short copolymer PS-b-PAA 41.0-b-4.2 kDa has a diameter of 80 nm in DBP. The long copolymer PS-b-PAA 197.0-b-190 kDa in DBP has a small percent around 200 nm and the majority around 3000 nm. It suggests that the long copolymer molecules aggregate. It is interesting to compare PS 35 kDa and

PS-b-PAA 41.0-b-4.2 kDa as they have similar PS and the PAA block of the copolymer is short. The copolymer is more than twice as big as the homopolymer in DBP, confirming that adding a solvophobic block has an effect on the size and might lead to polymer aggregation.

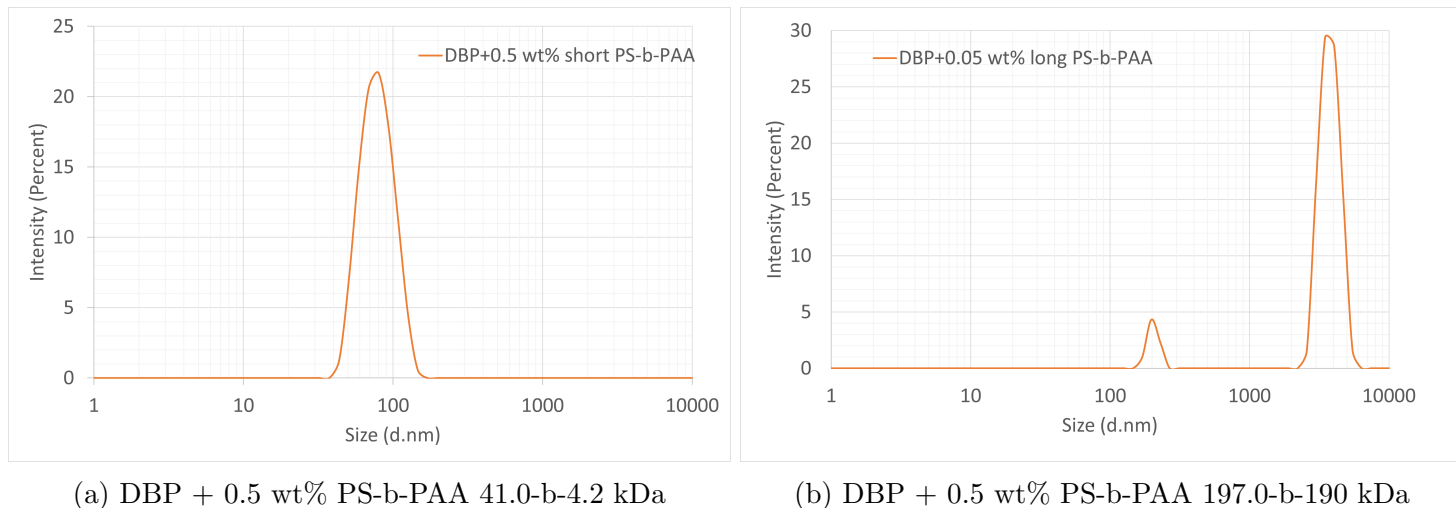
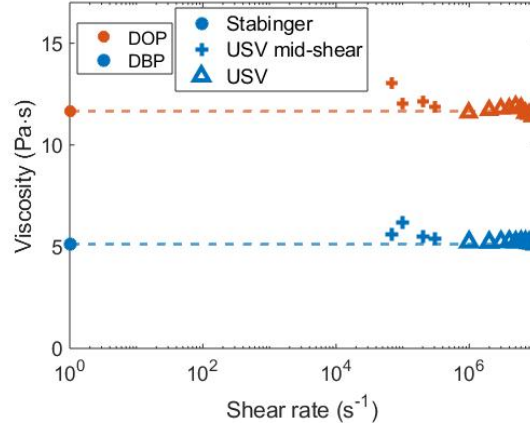


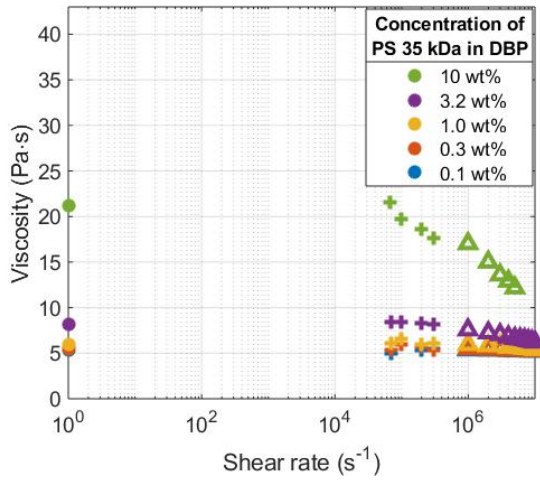
Figure 4.11: Distributions of the size of the copolymer molecules in DBP at 25 °C. Measurements performed by Amran Mohamed

4.3.5 Flow curves of the polymer solutions

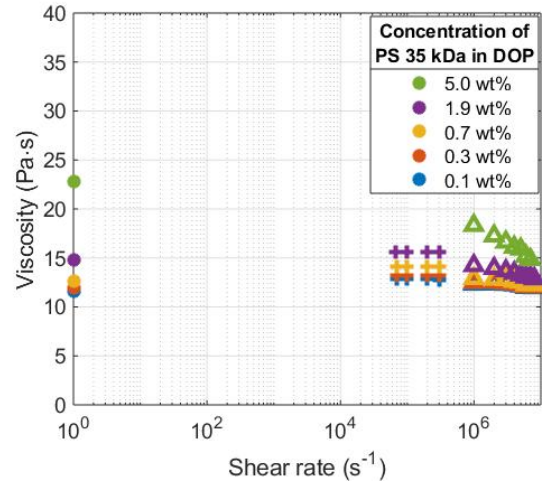
Viscosity measurements were conducted to determine the behaviour of the fluids under shear. The low shear viscosity was measured with a Stabinger viscometer (Anton Paar), the mid-shear and high-shear viscosity with a USV (PCS Instruments) (method in section 3.3). The results for DBP, DOP, DBP + PS 35 kDa, DOP + PS 35 kDa, DBP + PS 192 kDa and DOP + PS 192 kDa are given in figure 4.12. The minimum temperature accessible with the USV rig for these fluids was 60 °C due to their high viscosity. At lower temperatures, the torque exceeds the maximum torque the USV can sustain. DBP and DOP do not shear thin in the range of shear rates accessible with the USV (up to 10^7 s^{-1} , figure 4.12a). Shear thinning behaviours were also observed for the PS 35 kDa polymer solutions, figures 4.12b and 4.12c. For PS 35 kDa in DBP, the reduction in viscosity occurs already at $7 \times 10^4 \text{ s}^{-1}$ for the highest polymer concentration of 10 wt%, and after $3 \times 10^5 \text{ s}^{-1}$ for lower concentrations. Similar results were obtained for PS 35 kDa in DOP.



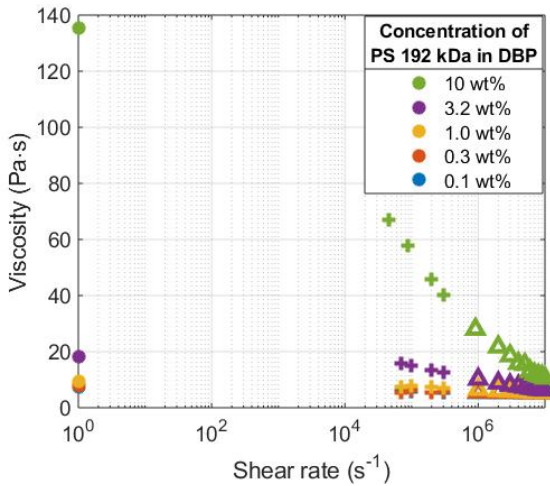
(a) DOP and DBP. The dashed lines represent the low shear viscosity.



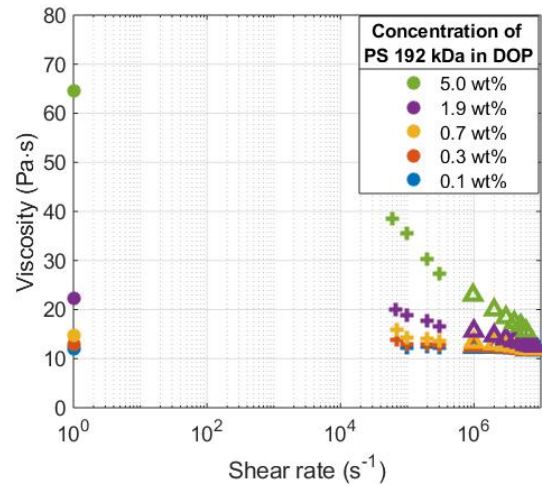
(b) DBP + PS $M_n = 35 \text{ kDa}$



(c) DOP + PS $M_n = 35 \text{ kDa}$



(d) DBP + PS $M_n = 192 \text{ kDa}$



(e) DOP + PS $M_n = 192 \text{ kDa}$

Figure 4.12: Viscosity at 60 °C as a function of shear rate for (a) DOP and DBP, (b) PS ($M_n = 35 \text{ kDa}$) in DBP, (c) PS ($M_n = 35 \text{ kDa}$) in DOP, (d) PS ($M_n = 192 \text{ kDa}$) in DBP, (e) PS ($M_n = 192 \text{ kDa}$) in DOP. Different symbols are used for the data points from the low-shear Stabinger viscometer (circles), the mid-shear USV (crosses) and high-shear USV (triangles).

Substantial shear thinning is observed for the PS 192 kDa polymer solutions in figures 4.12d and 4.12e, especially at high polymer concentrations (expected as high viscosity solutions experience higher shear stresses). For solutions of polymer concentrations above 0.7 wt%, the viscosity at the lowest shear rate ($7 \times 10^4 \text{ s}^{-1}$) is already lower than the low-shear viscosity. It can be concluded that for these polymer solutions, shear thinning is induced by the polymer and not the solvent, and that a higher polymer molecular weight leads to a more severe shear thinning, both in terms of reduction in the viscosity and in terms of the shear rate at which the shear thinning starts. Note that the critical shear rate is around $10^4 - 10^5 \text{ s}^{-1}$.

4.3.6 Film thickness of the polymer solutions

The decrease in viscosity of the polymer solutions due to shear thinning reduces their viscosity-thickening ability under shear. It might also impact the film thickness in the contact as a lower viscosity at the inlet would lead to a lower film thickness. Figure 4.13 shows the film thickness measured by interferometry for DBP + 9.9 wt% PS 192 kDa and DOP + 4.8 wt% PS 192 kDa at a SRR of 0 % and -180 % (ball faster). Pure sliding with the ball rotating (SRR -200 %) could not be achieved due to the limitations of the EHD2 rig (trigger on the disc). The film thickness is noticeably lower at higher SRR (in red) than in pure rolling (in blue). At the speed of interest 0.3 m/s, there is a decrease in the film thickness of DBP + 9.9 wt% PS 192 kDa of more than 50 nm (-30 %) between a SRR=0 % and a SRR= -180 %. Note that the change in film thickness with SRR might be due to shear thinning but also to shear heating. The film thickness of polymer solutions will be investigated in more details in section 5.2.

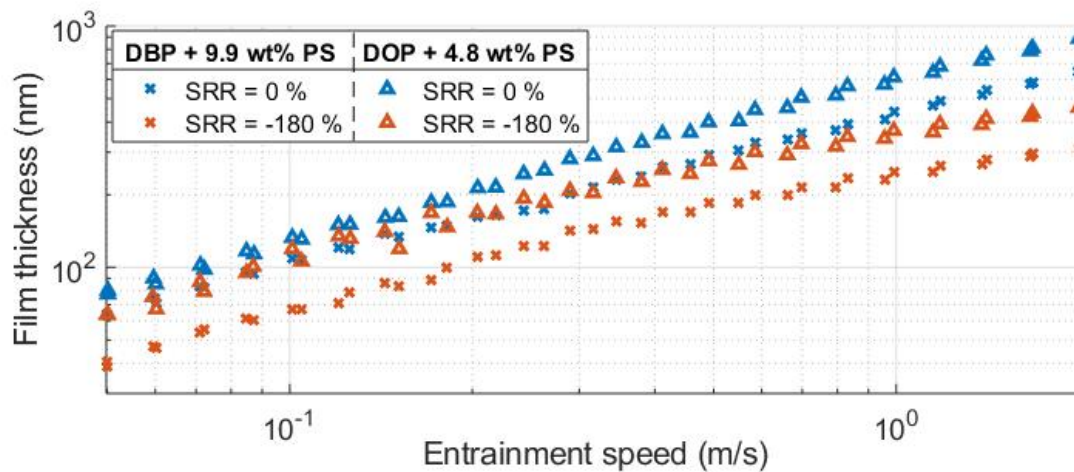


Figure 4.13: Film thickness of DBP + 9.9 wt% PS 192 kDa and DOP + 4.8 wt% PS 192 kDa, at SRR = 0 % (blue) and -180 % (red), $T=21 \text{ }^{\circ}\text{C}$ and $P_{max} = 418 \text{ MPa}$, steel ball against glass disc contact.

Comparison with prediction is not straightforward as the viscosity-pressure coefficients α of the polymer solutions are not known. The film thickness of DOP + 4.8 wt% PS 192 kDa in pure rolling is copied in figure 4.14 and compared to three predictions using Chittenden (equation 7.8), calculated with different viscosity-pressure coefficients and viscosities. Using the viscosity-pressure coefficient of neat DOP, $\alpha=16.7 \text{ GPa}^{-1}$, and the low-shear viscosity of the polymer solution, $\eta=0.44 \text{ Pa}\cdot\text{s}$, the prediction overestimates the film thickness (dotted red line). The prediction can be adjusted by changing the viscosity-pressure coefficient or the viscosity. Keeping the low-shear viscosity of $\eta=0.44 \text{ Pa}\cdot\text{s}$, $\alpha=3.5 \text{ GPa}^{-1}$ gives the best agreement with experimental measurements. However, this viscosity-pressure coefficient is too low to be realistic. Since the polymer solution most probably shear thins at the inlet, another calculation was done with a lower viscosity. The best agreement was found for $\eta=0.15 \text{ Pa}\cdot\text{s}$. This loss of viscosity is unrealistic. Note that a drop in viscosity at the inlet may also be due to shear-heating and polymer depletion. These calculations do not represent a rigorous method to estimate the film thickness but aim at highlighting the difficulty of predicting the film thickness in the case of polymer solutions.

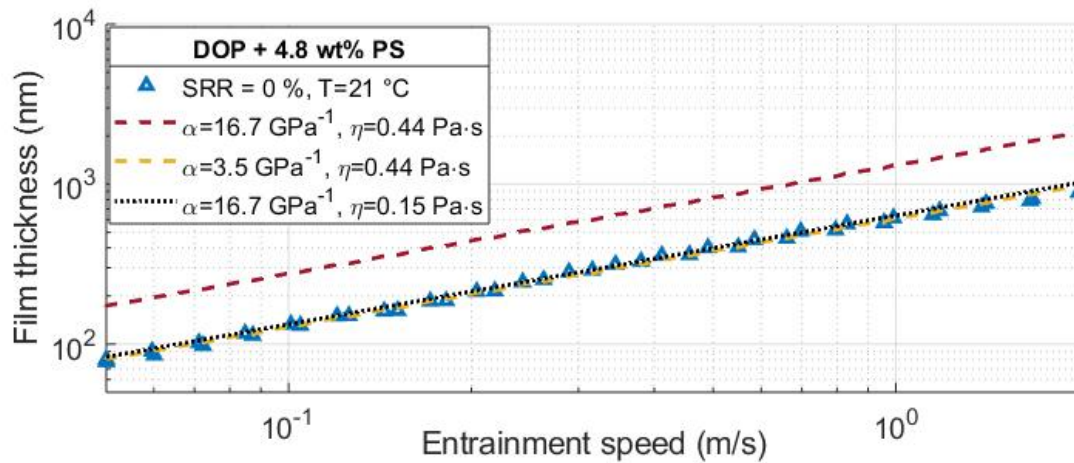
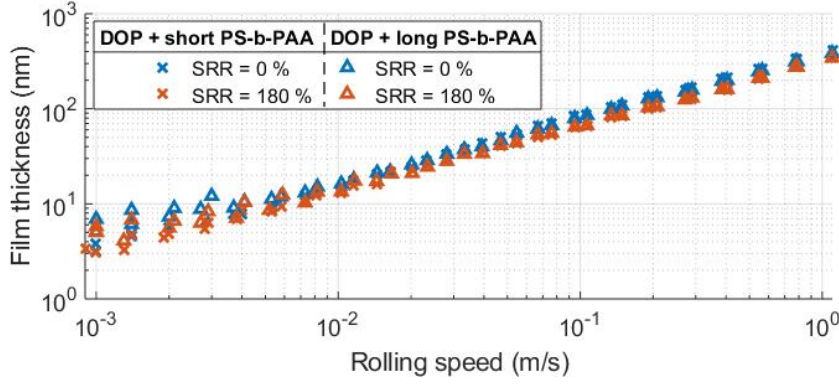
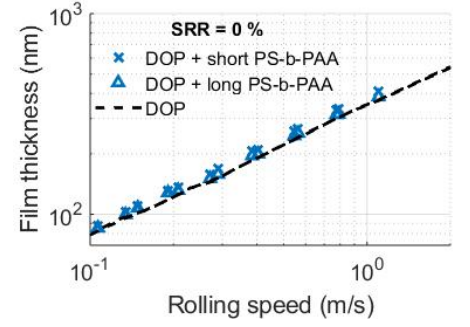


Figure 4.14: Film thickness of DOP + 4.8 wt% PS 192 kDa, at SRR = 0 %, T=21 °C and $P_{max} = 418 \text{ MPa}$, steel ball against glass disc contact. Dotted lines are predictions using Chittenden (equation 7.8).

The film thickness of the copolymer solutions is in figure 4.15. The two solutions, DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa (short copolymer) and DOP + 0.05 wt% PS-b-PAA 197.0-b-190 kDa (long copolymer) have a similar film thickness at room temperature. Increasing the SRR to 180 %, the film thickness is reduced negligibly. A comparison with DOP, in figure 4.15b, shows that there is little difference between the 3 fluids in the region of the speed of interest (0.3 m/s). This indicates that the conditions at the inlet of the contact are not changed by the polymer.



(a) at SRR = 0 % and 180 %



(b) Comparison with neat DOP, SRR=0 %

Figure 4.15: Film thickness of DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa (short) and DOP + 0.05 wt% PS-b-PAA 197.0-b-190 kDa (long), at room temperature and $P_{max} = 418 \text{ MPa}$, steel ball against glass disc contact.

If there is adsorption of the copolymer molecules or presence of micelles, it does not impact the film thickness under these conditions. Note that the addition of the copolymer has a negligible effect on viscosity at these low concentrations. The low shear viscosity at 25 °C measured using a SVM 3000 Stabinger viscometer (Anton Paar) is 58 mPa·s for DOP and 60 mPa·s for DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa (short copolymer). The viscosity of DOP + 0.05 wt% PS-b-PAA 197.0-b-190 kDa was not measured due to the difficulty to prepare the solution.

4.3.7 Adsorption of the polymer solutions

The adsorption of polymer and copolymer molecules on the contact surfaces was studied with a quartz crystal microbalance (QCM). In the QCM, the test fluid flows on a quartz crystal coated with silicon oxide. Adsorption of the molecules on the crystal will induce a shift of resonance frequency of the crystal, by which the adsorbed mass can be estimated [167]. Note that QCM only allows relatively thin fluids to be tested. The viscosity of DOP is higher than the maximum viscosity at which the QCM can operate. Thus, only the adsorption of DBP solutions was investigated.

All the QCM tests were performed by Amran Mohamed. The experiments were carried out at a temperature of 40 °C and a flow rate of 0.1 mL/s, using a Q-Sense E1 from Biolin Scientific.

The procedure for each QCM test was the following:

- The frequencies of toluene were obtained for 15 minutes, and were used as the reference
- The fluid of interest was run in the QCM for 15 minutes

- To evaluate if the adsorbed molecules were strongly attached to the crystal, toluene was run again for 15 minutes to remove loosely bound polymers

The results for DBP and DBP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa can be found in figure 4.16, which shows the change in mass on the QCM crystal over time. Using toluene as the baseline (stage 1), the mass adsorbed on the crystal is estimated. Stage 2 is the adsorption of DBP in DBP. DBP adsorbs on the crystal as indicated by the change of mass (stage 2). The adsorption is very quick as the mass jumps to a higher value and is then stable with time. When rinsed with toluene (stage 3), the mass goes back to a low value, which indicates that the DBP molecules do not strongly interact with the surface and are easily removed. In this stage 3, the mass does not go back to the initial value of stage 1, indicating that some DBP molecules remain on the surface. The toluene rinse is followed by stage 4, where the copolymer solution DBP+PS-b-PAA is flowed on the crystal. The mass obtained for the copolymer solution is higher than for neat DBP, and stable with time (stage 4). This indicates that the copolymer, or the copolymer along with DBP, adsorb on the crystal. During the final rinsing with toluene (stage 5), the mass decreases but keeps a relatively high value. This suggests that the copolymer molecules, or a combination of the copolymer and the solvent, adsorb on the surface, and that the interaction with the surface is strong.

Similar conclusions are drawn for the solutions with homopolymer polystyrene (results not shown here).

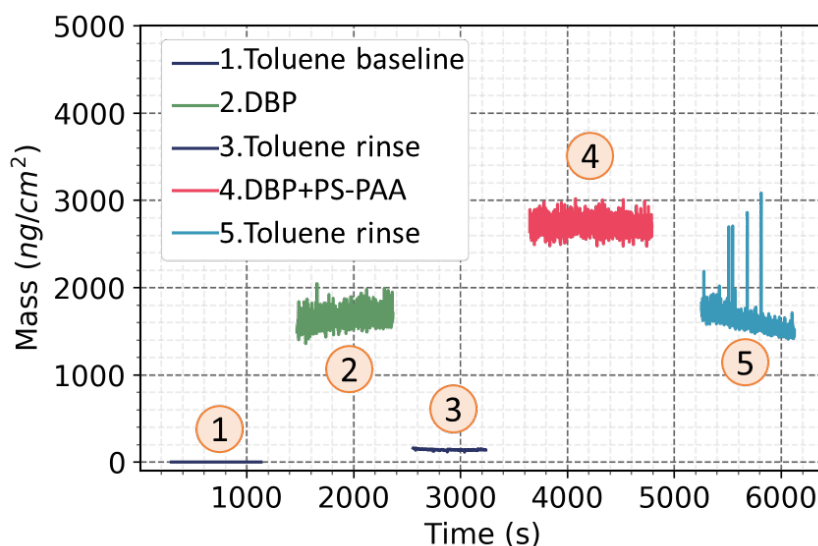


Figure 4.16: Mass adsorbed on QCM crystal over time. Toluene is the baseline. Test fluids are DBP and DBP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa. From Amran Mohamed.

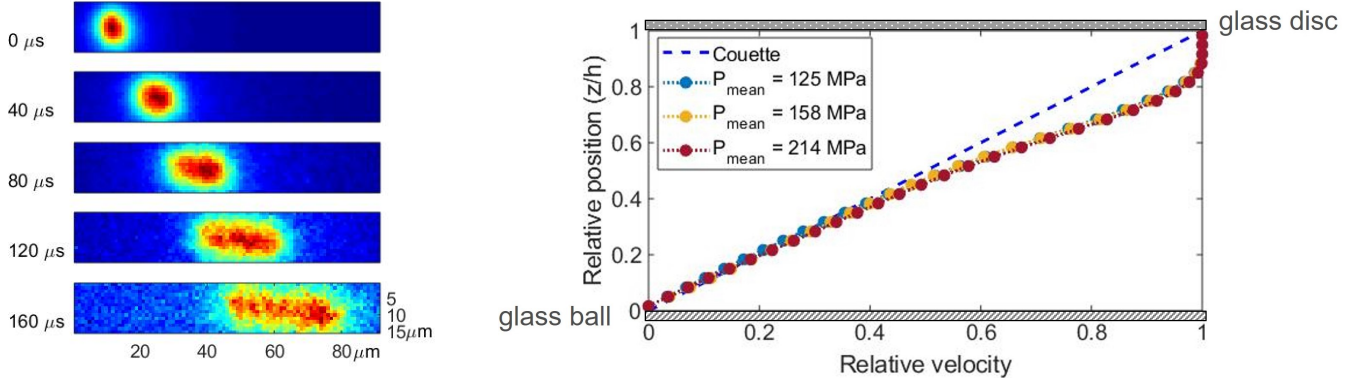
4.4 Results and discussions

4.4.1 Proof of concept - velocity profile of a neat oil, TOTM

Experiments with TOTM were carried out before the background correction procedure was implemented. Consequently, the results are analysed with care as the phosphorescence from the contact surfaces can create artefacts in the reconstructed velocity profiles. The consequence is that, depending on the intensity from the surfaces, the boundary conditions are forcibly stick and not slip (correctly or incorrectly) and that artificial velocity plugs of the fluid at the surfaces might be observed. Therefore, only experiments with a high film thickness, where the conditions are mild (low pressure and low temperature), are presented for TOTM in this section. A high film thickness leads to a higher signal-to-noise ratio as the phosphorescence intensity from the fluid increases when the thickness increases, limiting artefacts from the phosphorescence of the contact surfaces. The film thickness was kept well under the depth of field of the objective ($1.1\ \mu\text{m}$) to ensure that the whole film was within the depth of field and captured accurately.

Figure 4.17 shows the phosphorescence images over time and the reconstructed velocity profiles for TOTM. The specimens used were a glass ball and a glass disc. The experimental conditions for these tests were an entrainment speed $U_e=0.3\ \text{m/s}$, a temperature $T=30\ ^\circ\text{C}$, a slide-roll ratio $SRR = 50\ \%$ (disc faster) and three different mean contact pressures of 125 MPa, 158 MPa and 214 MPa. Under these conditions, the central film thickness is $h_c = 320\ \text{nm}$ (measured with the EHD2 by PCS Instruments). The phosphorescence response suggests a Couette response as the intensity spreads rather homogeneously when the fluid is sheared. The reconstructed velocity profiles confirm a near-Couette velocity profile, with a small deviation at the fast surface (the disc). Due to the absence of background correction and the low intensity of the dye response, it is not possible to conclude if the deviation is real or if it is indeed a Couette flow. However, comparing the results at three different pressures, it can be noted that a small change of pressure at low pressure does not affect the velocity profile of TOTM. This was anticipated as for TOTM, no change within the fluid such as a glass transition is expected at these low pressures. These initial results confirm the feasibility of the technique.

Knowing that this phosphorescence velocimetry imaging technique is reliable and can be used to investigate the through-film behaviour of fluids in a tribological contact, it is used to reconstruct velocity profiles of complex solutions of lower film thickness. In the next sections, results for polymer solutions are presented.



(a) Phosphorescence images at $P_{mean} = 125 \text{ MPa}$ (b) Velocity profiles at different contact pressures

Figure 4.17: Phosphorescence images and velocity profiles for TOTM, $U_e=0.3 \text{ m/s}$, $T=30^\circ\text{C}$, $SRR = 50 \%$ (disc faster), glass ball against glass disc.

4.4.2 Velocity profiles of polymer solutions

In this section, results for the solutions DBP + 9.9 wt% PS 192 kDa and DOP + 4.8 wt% PS 192 kDa are presented. Table 4.4 shows the characteristics of the test solutions. The low-shear dynamic viscosity was measured using a SVM 3000 Stabinger viscometer (Anton Paar), and the film thickness was measured by optical interferometry using an EHD2 rig (PCS Instruments). The film thickness was also measured at other SRRs, up to a SRR of 180 % (see figure 4.13). It is interesting to notice that while having a higher low-shear viscosity, the solution DOP + 4.8 wt% PS 192 kDa has a lower film thickness than DBP + 9.9 wt% PS 192 kDa. As studied in section 4.3.5, both solutions shear thin extensively and already at the lowest shear rate measured, $7 \cdot 10^4 \text{ s}^{-1}$. Even though these flow curves were obtained at 60°C and could not be obtained at room temperature as the viscosity of the solutions was too high, the polymer solutions are likely to shear thin at room temperature, and at lower shear rates since they are more viscous at room temperature. The comparison of the film thickness of DBP + 9.9 wt% PS 192 kDa and DOP + 4.8 wt% PS 192 kDa gives an indication on the severity of the shear thinning experienced by these solutions: it is likely that DBP + 9.9 wt% PS 192 kDa undergoes a more severe viscosity drop at the inlet, as while having a higher low-shear viscosity, its film thickness is lower. Surprisingly, the film thickness of DOP is slightly reduced at high SRR. DOP does not shear thin under these conditions, as seen in figure 4.12a. The lower film thickness at $SRR = -180 \%$ might be attributed to shear heating.

The velocimetry experiments were carried out at room temperature and under pure sliding conditions, where the disc was stationary and the ball rotated. Figure 4.18 shows the phosphorescence images and the reconstructed velocity profiles for neat DOP (figure 4.18a) and for the two polymer solutions (figures 4.18b and 4.18c). All the images

were background corrected and each image is normalised individually.

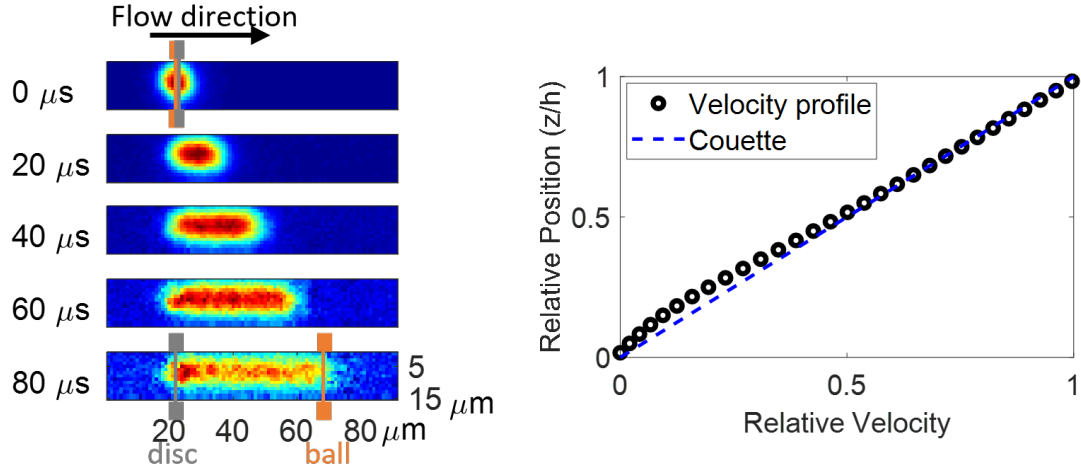
Table 4.4: Polymer solutions characteristics

Solution	Polymer concentration	Solution viscosity at 25 °C	Film thickness at 25 °C, 0.3 m/s	
			0 % SRR	-180 % SRR
DOP	N/A	58 mPa·s	150 nm	138 nm
DOP+PS	4.8 wt %	349 mPa·s	235 nm	187 nm
DBP+PS	9.9 wt %	643 mPa·s	185 nm	127 nm

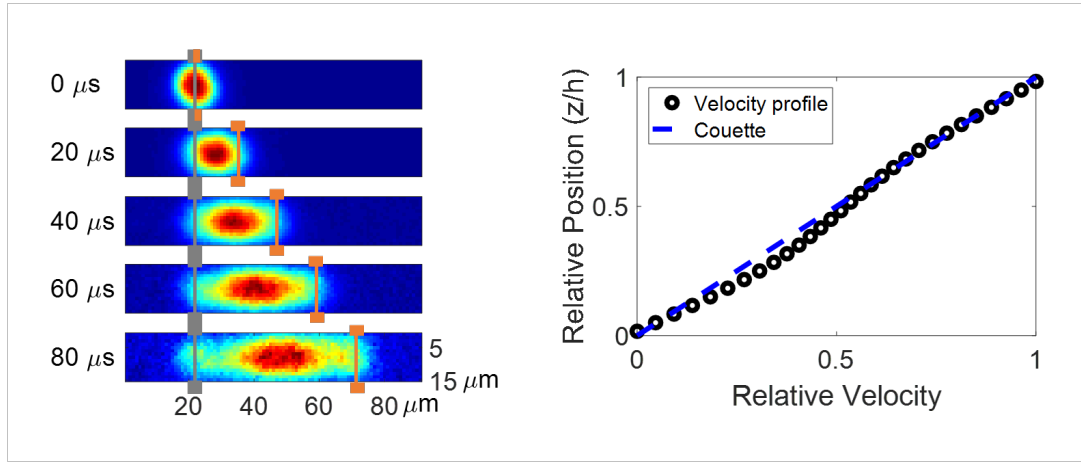
No slip is observed for DOP (figure 4.18a) and DOP+PS (figure 4.18b). In both cases, the velocity of the fluid at the surfaces is the same as the velocity of the surfaces. On the other hand, the DBP+PS solution (figure 4.18c) exhibits a clear slip at both contact surfaces. The velocity profile shows that at the proximity of the stationary disc surface (relative position is 0), the relative velocity of DBP+PS is not zero; and at the ball surface (relative position is 1), it is less than 1, i.e. the fluid moves more slowly than the ball. It can be noted that the average velocity of the solution is higher than the relative entrainment speed of 0.5, as slip occurs more at the slower surface (the disc). This participates in a reduction of film thickness [117]. The question arises as to why one system, DBP+PS, gives slip, whereas the other two solutions, DOP and DOP+PS, do not.

One possible slip mechanism is depletion, in which the solute goes away from the wall, creating a gradient in the polymer concentration and thus in the viscosity through the thickness of the film [119]. However, this mechanism is very unlikely to be at play here, as Grzelka *et al.* [163] showed that for a DEP+PS system (DEP has a similar chemistry as DBP and DOP, its end chains are two and three carbons shorter, respectively), the friction coefficient at the wall strongly depends on the polymer volume fraction, ruling out the possibility of a depletion layer at the wall. Knowing this, coupled with the fact that the DBP+PS solution has a higher viscosity, it can be assumed that this solution slips at the wall because it experiences a higher shear stress, leading to more slip than the solution DOP+PS. Results under other experimental conditions would be needed to confirm this hypothesis. Another possible reason is that DBP might have more mobility at the surface, as molecules of DBP are smaller than molecules of DOP. A higher mobility at the surface promotes slip [168].

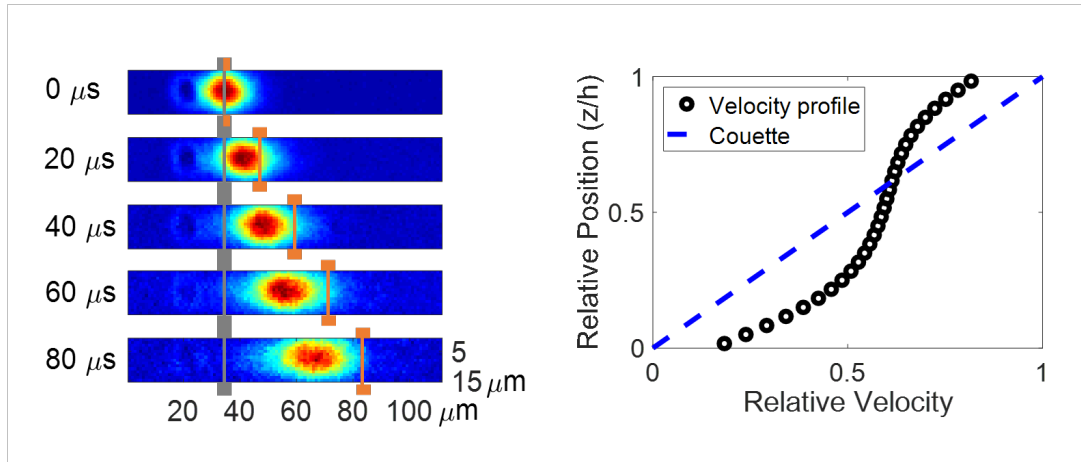
Note that DOP and DBP may interact with the surface (as suggested by their no-slip flow profiles), even though they may have different adsorption strengths. Since molecules of DBP are smaller than molecules of DOP, PS may displace adsorbed DBP more readily than adsorbed DOP. This implies that the solid-liquid interface may be different in the two cases. A higher concentration of polymer [163] and a higher polymer surface coverage [169] might facilitate slip.



(a) DOP



(b) DOP + 4.8 wt% PS 192 kDa



(c) DBP + 9.9 wt% PS 192 kDa

Figure 4.18: Background corrected and normalised phosphorescence images, and velocity profiles. The first image is taken as the time reference. Grey lines and orange lines represent the position of the disc and the ball, respectively. Dashed lines in velocity profiles correspond to a Couette flow. All three tests are done in pure sliding, with $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C.

4.4.3 Velocity profiles of copolymer solutions

The flow behaviour of PS-b-PAA copolymer solutions was also investigated. Based on the adsorption results (section 4.3.7), PS-b-PAA adsorbs more easily and potentially forms micelles (see DLS results section 4.3.4). So these copolymer solutions might have different flow profiles from PS solutions.

The copolymers selected being expensive and difficult to dissolve, a concentration of 0.5 wt% in DOP was used for the short copolymer PS-b-PAA 41.0-b-4.2 kDa and only less than 0.05 wt% of the long copolymer PS-b-PAA 197-b-190 kDa could be dissolved in DOP. These are low concentrations for viscosity modifiers, which would typically be in a concentration ranging around 2-5 %. Due to the low concentration of the copolymers, the change in viscosity of the solutions was negligible. Consequently, only experiments with DOP as a solvent could be carried out, as DBP was too thin. The viscosity and film thickness of the copolymer solutions are reported in table 4.5.

Table 4.5: Copolymer solutions characteristics

Solution	Polymer concentration	Solution viscosity at 25 °C	Film thickness at 25 °C, 0.3 m/s, 0 % SRR
DOP	N/A	58 mPa·s	150 nm
DOP+PS-b-PAA 41.0-b-4.2 kDa	0.5 wt%	60 mPa·s	180 nm
DOP+PS-b-PAA 197-b-190 kDa	0.05 wt%	-	158 nm

The phosphorescence images and the velocity profiles for these copolymer solutions are shown in figure 4.19. The ones for DOP are also reproduced in the figure, for easier comparison. The two sets of images, figures 4.19b and 4.19c, clearly show a difference in the phosphorescence response. In the case of DOP (figure 4.19a), the intensity is relatively even in the direction of the flow. With the copolymer solutions, two bright spots can be seen on the contact surfaces (on the left for the stationary disc, and on the right for the rotating ball). For DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa only (figure 4.19b), a slightly brighter region in between the two surfaces. The corresponding velocity profiles in figure 4.19d exhibit two plugs at the contact surfaces (relative velocity of 0 for the disc and 1 for the ball) for both copolymer solutions, which is consistent with the phosphorescence responses. For DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2, a change of slope corresponding to the brighter central part is also noticed.

The adsorption of the copolymers on the contact surfaces might cause the inhomogeneous shear behaviour. Adsorbed polymer molecules might create layers of higher viscosity at the interfaces, leading to the plugs in the velocity profile; layers in which the fluid experiences a low strain rate. It can also be noticed that the plug at the ball interface is bigger than the plug at the disc interface for both copolymer solutions. This might be due to thermal effects. The disc is stationary so the heat at this surface

builds up more quickly than at the ball, which rotates and moves the heat away from the contact. A higher temperature means that the local viscosity at the disc interface is lower. Studies on friction modifiers support the hypothesis that adsorbed molecules are linked to inhomogeneous shear behaviour. Ewen [170] observed, with numerical simulations, plugs of constant velocity in the layer of adsorbed organic friction modifier molecules. However, this has to be considered with care as in the case of friction modifiers, the tribological contact is in the mixed or boundary regime, whereas this work is done in the elastohydrodynamic regime.

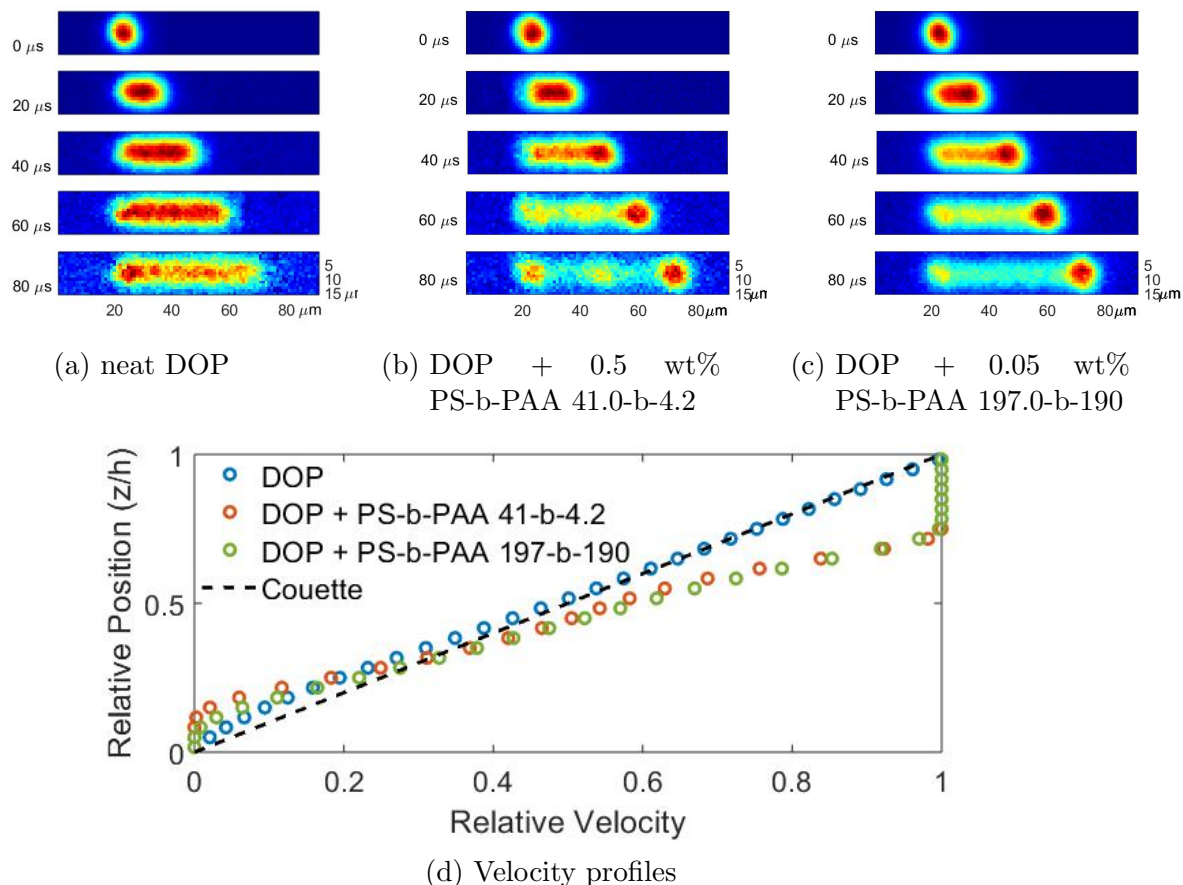


Figure 4.19: DOP, DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa and DOP + 0.05 wt% PS-b-PAA 197-b-190 kDa, in pure sliding (ball rotates), with $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C. (a), (b) and (c) are background corrected phosphorescence images, direction of the flow is left to right, (d) are the corresponding reconstructed velocity profiles.

To assess the effect of adsorption time on the velocity profile, two experiments are performed and compared, using DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa. One is done with clean specimens and run as quickly as possible once the copolymer solution is poured in the rig and in contact with the surfaces. For the second experiment, the specimens are immersed overnight in the copolymer solution before running the test. The phosphorescence images are in figure 4.20a for the first case (no pre-exposition) and in

figure 4.19b for the second case (specimens immersed overnight). The two corresponding velocity profiles are compared in figure 4.20b. The phosphorescence images show a slightly brighter spot on the disc (left side of the phosphorescence response in figure 4.19b) after overnight immersion, which suggests that a more viscous layer may have formed. However, the reconstructed velocity profiles are very similar. The difference between the two cases is too small to be conclusive.

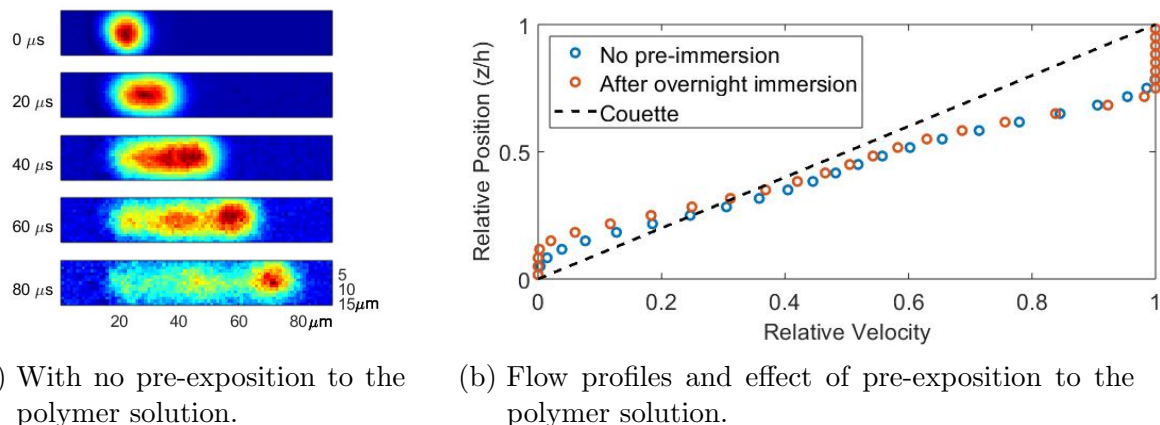


Figure 4.20: DOP + 0.5 wt% PS-b-PAA 41k-b-4.2k, in pure sliding, with $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C.

To evaluate the effect of which surface (ball or disc) rotates faster, a test at a SRR of +180 % (disc faster) was performed. A SRR of +200 % could not be achieved as the fluid is entrained in the contact when the ball rotates. At SRR = +200 %, the ball is stationary and the contact starves. The velocity profile is reported in figure 4.21 and compared with the previous result obtained at a SRR of -200 %. The two velocity profiles are very similar, the bigger plug is located at the fast surface, which is the colder surface (the ball for SRR=-200 % and the disc for SRR= +180%). The surface that rotates faster removes more heat coming from the shearing of the fluid, creating a local layer of higher viscosity in the fluid near the surface.

Lower SRR could not be tried as the lower the sliding speed, the longer the time needed to obtain a minimum travel distance of the dye molecules of 30 μm (minimum distance to be able to discriminate the two contact surfaces in the phosphorescence response). The intensity was too low and decreasing too rapidly to reach this requirement.

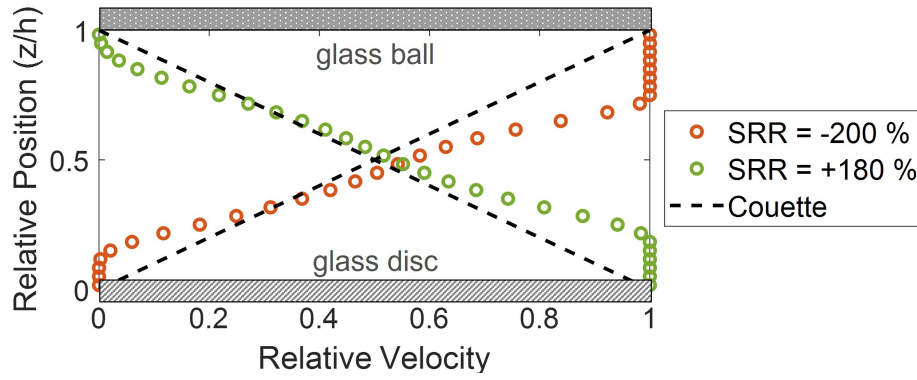


Figure 4.21: Comparison of flow profiles at SRR of +180 % (disc faster) and -200 % (ball faster), DOP + 0.5 wt% PS-b-PAA 41.0-b-4.2 kDa, with $P_{max}=188$ MPa, $U_e=0.3$ m/s and $T=25$ °C.

4.5 Conclusions

Velocity profiles and interfacial slip of polymer and copolymer solutions in the elastohydrodynamic regime were investigated by a phosphorescence imaging velocimetry technique which allowed *in situ* observations of flow behaviours at the microscopic scale.

Velocity profiles of DBP+PS and DOP+PS were successfully reconstructed from phosphorescence images of the tribological contact. Both DBP and DOP obey the no-slip boundary condition and give Couette flow profiles, while slip is observed with DBP + 9.9 wt% PS 192 kDa. No slip is observed for DOP + 4.8 wt% PS 192 kDa. Possible explanations for the difference in behaviours between the two polymer solutions were proposed, though more work is needed to discriminate the effect of the solvent and the effect of the polymer concentration. Future work should include the exploration of other possible reasons for the low film thickness, as well as the study of the impact of pressure and film thickness as they play a role in slip [147] and flow profiles [24].

Velocity profiles of block copolymer solutions DOP + PS-b-PAA were also obtained. The results suggest that the adsorption of the copolymer on the contact surfaces has an impact on the velocity profiles and induces inhomogeneity in the shearing behaviour of the fluid.

Chapter 5

In situ investigation of the composition of polymer solutions in a tribological contact in the elastohydrodynamic lubrication regime

In this chapter, chemical analyses of polymer solutions are performed *in situ* in a tribological contact in the elastohydrodynamic regime, using Raman spectroscopy. Results suggest that when the polymer molecules enter the tribological contact, no difference in polymer concentration is measured between the inside of the contact, its inlet or its outlet.

5.1 Introduction

The complexity of the flow and the rheology of polymer solutions in a tribological contact were discussed in chapter 4. The polymer solutions under investigation exhibited interfacial slip, their velocity profiles deviated from a Couette flow. The study of the properties of polymer solutions is extended in this chapter. Utilising low viscosity lubricants to reduce energy waste through lower friction while ensuring a thick enough lubricant film has become a significant challenge. Viscosity modifier additives help to maintain a good viscosity of the lubricant at high temperature, so a reasonable film thickness can be achieved. However, there is minimal knowledge on how film thickness is affected by the behaviour of polymeric solutions at the microscopic scale, such as polymer adsorption or polymer aggregation at the inlet.

This chapter aims to answer the following questions:

- *What are the possible mechanisms driving the film thickness of polymer solutions in a tribological contact under the elastohydrodynamic regime? Do polymer solutions experience shear thinning, polymer depletion or polymer aggregation?*
- *Do polymer molecules enter the contact?*

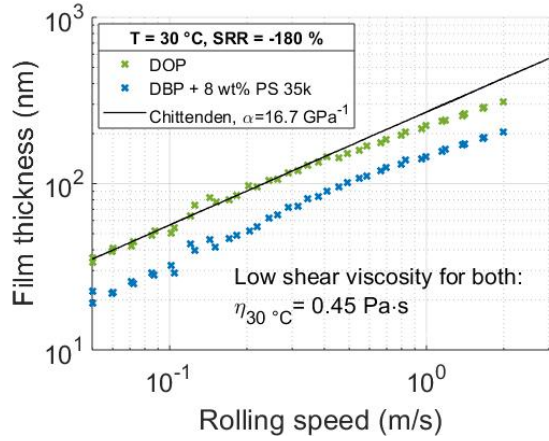
A novel *in situ* technique using Raman spectroscopy is developed to perform chemical analysis in a contact. This technique is designed to track potential changes in the polymer concentration in the contact and at the inlet, caused by polymer aggregation or polymer depletion. The results will confirm if polymer molecules enter the tribological contact or if there is polymer depletion near the inlet. The effects of concentration and slide-roll ratio will also be investigated.

5.2 Film thickness of polymer solutions

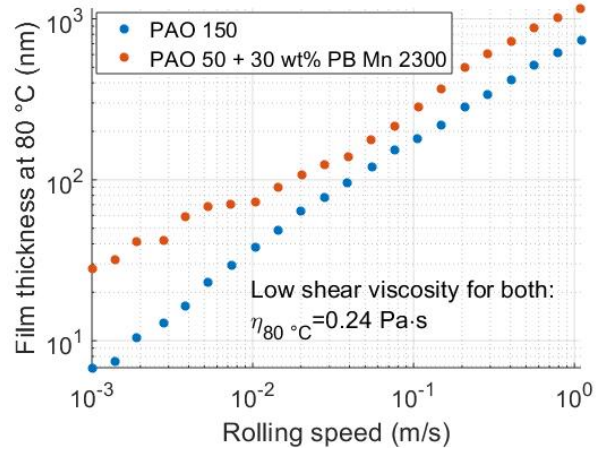
The reader can refer to section 2.9 for details on the existing work on the film thickness of polymer solutions. When measured experimentally, the film thickness of polymer solutions in a tribological contact is usually different than expected based on its low shear viscosity or from theoretical calculations, and can be either thicker or thinner.

The film thickness is driven by the viscosity at the inlet of the contact. So the film thickness of a polymer solution might be affected by a change of conditions at the inlet:

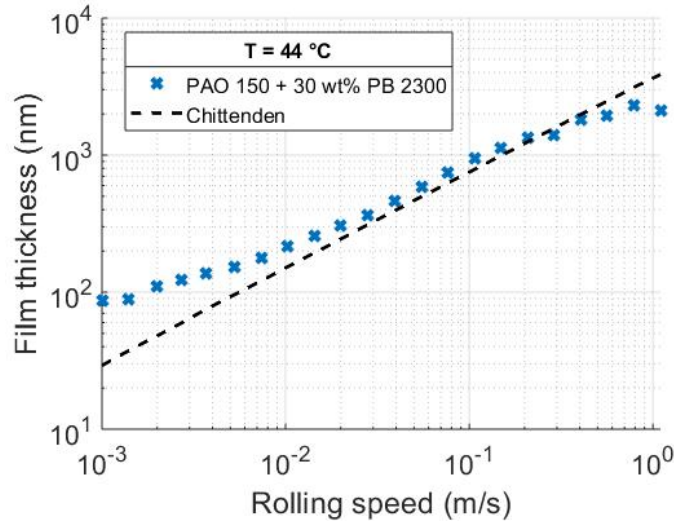
- shear thinning of the polymer or of the solvent at the inlet [171]
- any change in the entrainment speed in the contact due to a deviation of the lubricant flow from the no-slip, linear flow. For example, in the case of boundary slip, in order to maintain flow continuity, the film thickness increases when the slip occurs at the fast contact surface, and decreases when the slip occurs at the slow surface [117]
- polymer molecules sweeping around the contact [121]. Due to their size, polymer molecules might sweep around the contact or aggregate at the inlet instead. This would induce a change of the inlet viscosity, hence affect the film thickness
- adsorption of polymer molecules on the contact surfaces might also result in a higher concentration of polymer molecules at the inlet, hence a increased inlet viscosity [121].



(a) Lower film thickness for the polymer solution



(b) Higher film thickness for the polymer solution



(c) Comparison with estimation using Chittenden equation for film thickness [172]

Figure 5.1: Film thickness of polymer solutions

Figure 5.1 gives an illustration of how polymer additives change film thickness. In figure 5.1a, the polymer solution DBP + 8 wt% PS ($M_w = 35 \text{ kDa}$) has a lower film thickness than DOP, while both fluids have the same low shear viscosity. Note that the chemistries of DBP and DOP are similar (see figure 4.8 and 4.9a for their chemistries and table 4.1 for the properties of the phthalate esters). The film thickness of DOP matches well the theoretical calculation, with a slight deviation at high speed (from 0.6 m/s). DOP does not shear-thin, even at high shear rates (see section 4.3.5), the deviation in film thickness at high speed might be due to shear heating. As discussed in chapter 4, the film thickness of the polymer solution might be reduced due to interfacial slip. Film thickness can also be affected by inlet shear-thinning. In figure 5.1b, the film of the polymer solution, PAO 50 + 30 wt% polybutene ($M_n = 2300 \text{ Da}$), is thicker than that of

PAO 150 which is the neat oil of the same viscosity. Even though the test is performed under pure rolling conditions, the shear rate at the inlet might be high enough to induce shear-thinning of PAO 150. In this case, the different rheological responses of the two fluids might be due to different shear-thinning behaviours. Figure 5.1c is a comparison of the experimental measurement and the theoretical calculation of the film thickness of a polymer solution, PAO 150 + 30 wt% polybutene ($M_n = 2300 Da$). It can be noted that the thickness deviates at low speeds and is higher than the predicted value, suggesting adsorption of the polymer on the contact surfaces.

While inlet shear-thinning is commonly used to explain a reduction in film thickness, a change in polymer concentration at the inlet may give similar results. Raman spectroscopy has proven to be an effective method to study chemical changes [173, 174] and measure the concentration of solutes [175]. An novel *in situ* technique using Raman spectroscopy is hence developed to quantify polymer concentration in a tribological contact in the elastohydrodynamic lubrication regime.

5.3 Novel experimental setup and methodology

5.3.1 Polymer solutions and experimental conditions

One of the main limitations for this *in situ* Raman spectroscopy experiment is the intensity of the Raman scatter. In order to have a high enough signal-to-noise ratio, the central film thickness of the chosen system needs to be higher than $1.5 \mu m$ in the contact (see section 5.3.9 for more details). For this reason, the polymer solutions were made very viscous and a high concentration of polymer was used. The oils chosen were PAO 150 and PAO 50 from ExxonMobil, and two polybutene polymers (PB) were used: Indopol H-300 ($M_n = 1300 Da$) from INEOS Oligomers and a polybutene ($M_n = 2300 Da$) from Sigma-Aldrich. The chemistries of PAO and PB are shown in figure 5.2. Mixtures of different polymer concentrations were prepared by gently stirring for 3 days at $60^\circ C$. The dynamic viscosity of the fluids was measured with a Stabinger viscometer SVM-3000 (Anton Paar). The film thickness in a contact was measured by interferometry using an EHD2 (PCS Instruments). Table 5.1 lists the polymer solutions with their properties, as well as those of the solvents PAO 50 and PAO 150. More details on the film thickness measurements are given in section 5.3.6.

The specimens used were a steel ball and a sapphire disc. The experimental conditions are listed in table 5.2 and material properties in table 5.3.

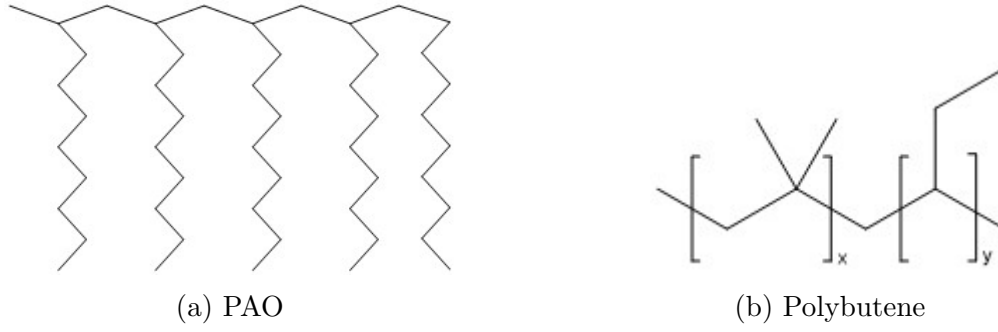


Figure 5.2: Chemistry of a typical PAO and polybutene

Table 5.1: Solvents and polymer solutions, dynamic viscosity and film thickness

polymer	oil	polymer concentration	dynamic viscosity at 25 °C (Pa·s)	central film thickness (μm) T=25 °C, $U_e = 0.3 \text{ m/s}$, $P_{max} = 526 \text{ MPa}$
	PAO 50	-	0.7	0.8
	PAO 150	-	3.9	1.9
polybutene $M_n = 1300 \text{ Da}$	PAO 50	30 wt%	2.1	1.8
		50 wt%	4.6	3.5
	PAO 150	30 wt%	5.7	3.1
polybutene $M_n = 2300 \text{ Da}$	PAO 50	30 wt%	4.3	2.5
	PAO 150	10 wt%	5.2	2.2
		30 wt%	8.1	2.8

Table 5.2: Experimental conditions for the Raman spectroscopy technique

Specimens	steel ball and sapphire disc
Entertainment speed U_e	0.3 m/s, 1 m/s
Temperature T	15 °C, 25 °C, 40 °C, 60 °C
Slide roll ratio SRR	-200 % (pure sliding, disc is stationary) 0 % (pure rolling)
Maximum pressure P_{max}	636 MPa
Hertzian contact radius	67 μm

Table 5.3: Material properties of specimens used in the Raman spectroscopy experiments

Material	Elastic modulus E (GPa)	Poisson's ratio ν
Glass	75	0.22
Sapphire	345	0.3

5.3.2 Home-built *in situ* Raman spectroscopy setup

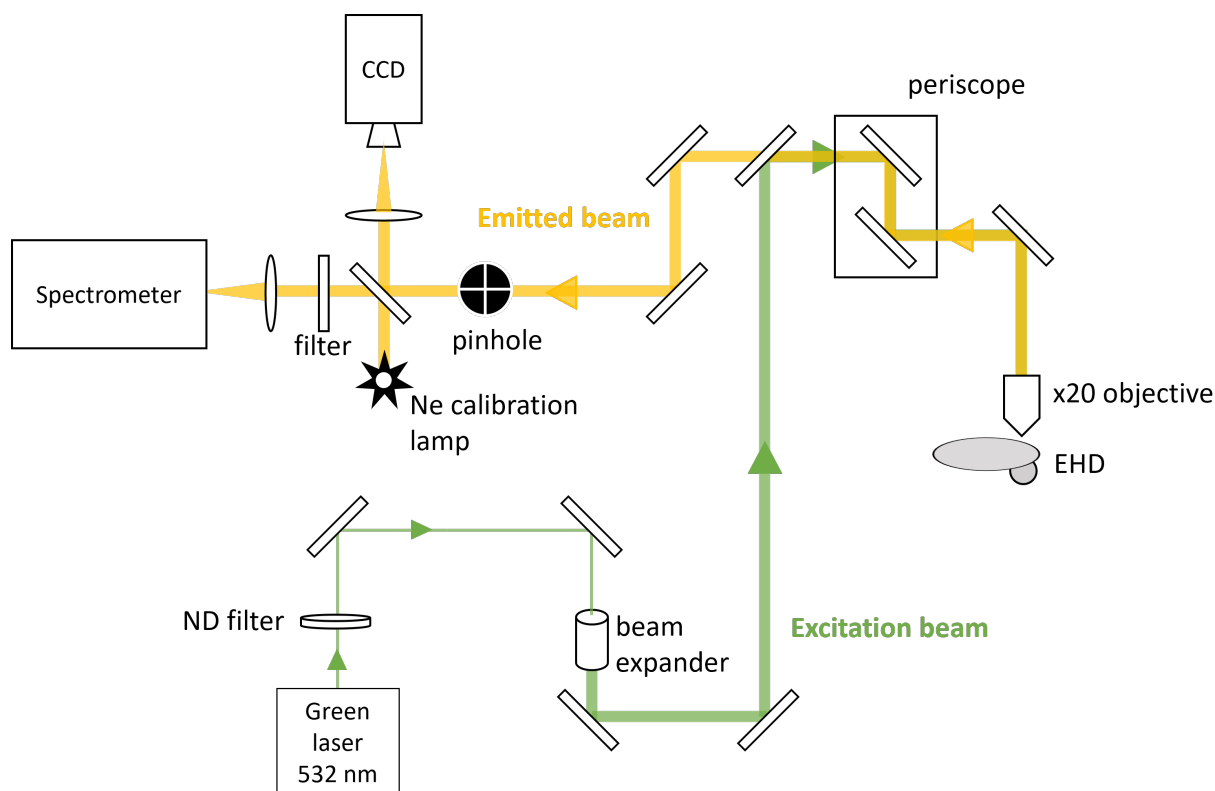


Figure 5.3: Schematic of Raman spectroscopy

A Raman spectroscopy setup was built to make *in-situ* chemical analysis in a ball-on-disc contact. A schematic of the setup and its optical components are given in figure 5.3. An EHD1 rig by PCS Instruments was used to create the tribological contact. The excitation source was a continuous green laser of wavelength 532 nm (model MLL-III-532/1 by CNI Laser). The tribological contact was imaged with a 20x objective (numerical aperture: 0.5, depth of field: $1.10\ \mu\text{m}$, working distance: 2.1 mm). The Raman scattered light was collected via the same objective to a SR-500i-C Andor spectrometer and the spectrum was recorded using a Andor iDus 401 CCD camera. In the EHD1 rig, a steel ball was immersed in a lubricant bath and pressed against a sapphire disc. Sapphire was chosen as this material is transparent, giving optical access to the contact, and does not have Raman peaks in the same range of wavenumbers as the polymer solutions. The load was controlled and kept under 10 N to prevent breaking the thin sapphire disc. The speeds of the ball and the disc were controlled independently. A cooler was mounted on the rig to reach temperatures down to 15 °C. The acquisition of Raman spectra were done using an exposure time of 0.97 s and with 100 accumulations.

The EHD1 rig was positioned on a X-Y motorised stage, to allow measurements to be taken at different positions across the contact by moving the rig under the microscope.

Measurements were typically done in the contact, at $400\ \mu\text{m}$ upstream (inlet) and $400\ \mu\text{m}$ downstream (outlet). Due to a strong cavitation, the signal-to-noise ratio was usually too low at the outlet to obtain usable Raman spectra. Figure 5.4 shows an image of a typical contact along with a schematic of the setup. The FWHM of the laser spot was smaller than $10\ \mu\text{m}$, as shown in figure 5.5. The laser spot was small compared to the size of the contact, the contact had a Hertz radius of $67\ \mu\text{m}$ at a load of $6\ \text{N}$.

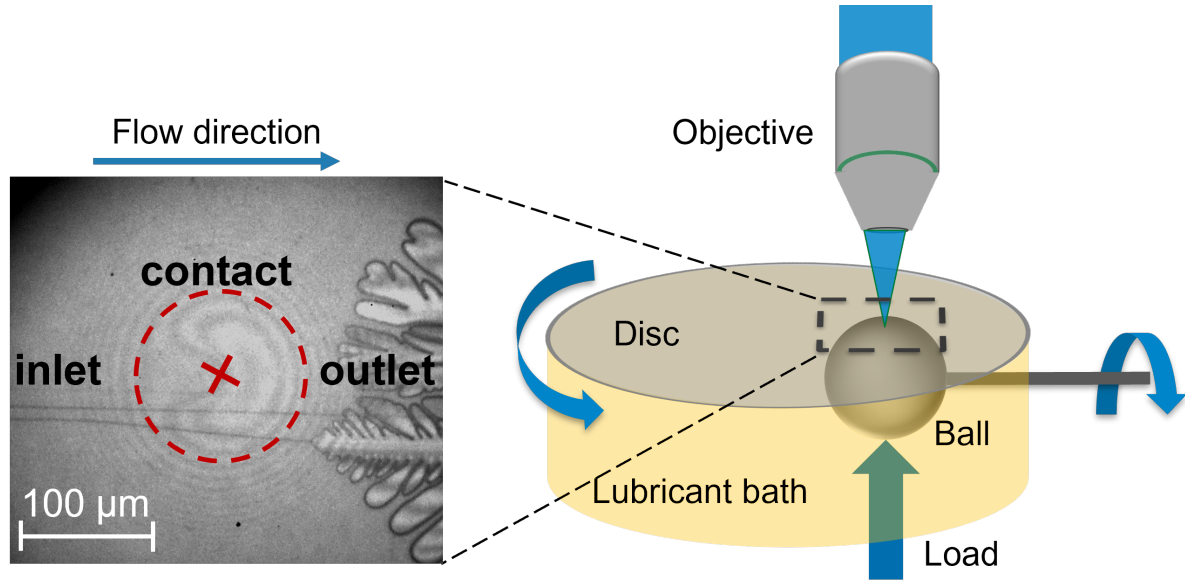


Figure 5.4: Schematic of the ball-on-disc contact with image of the contact. The red dashed circle highlights the contact, the red cross highlights the centre of the contact.

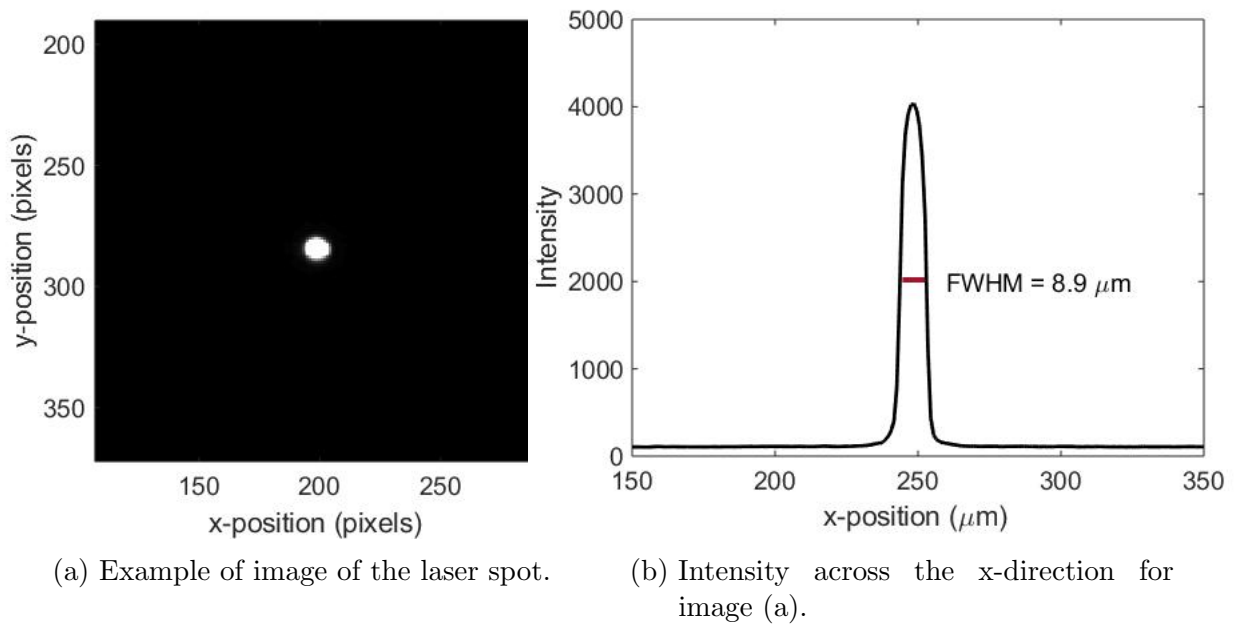
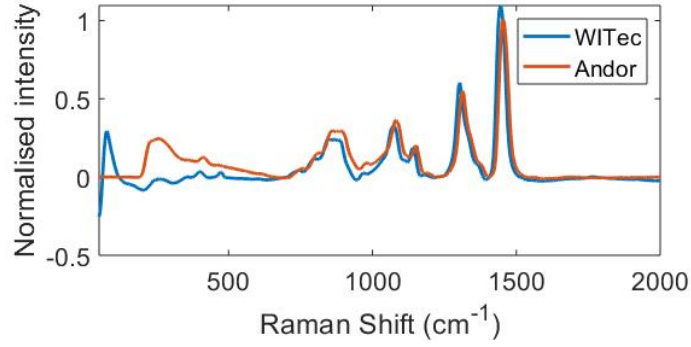


Figure 5.5: Laser spot in a loaded contact under static conditions.

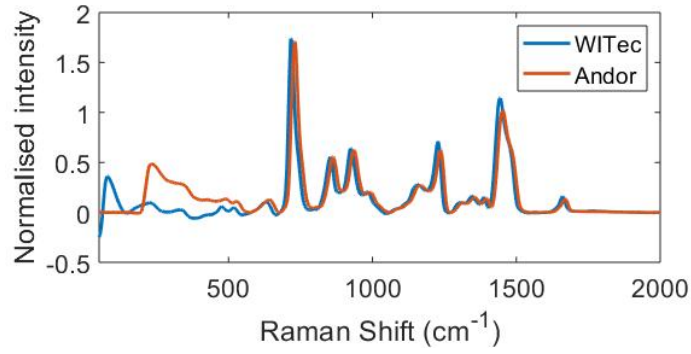
5.3.3 Validation of the Raman spectra

To confirm that the home-built Raman spectroscopy setup is giving reliable results, the Raman scatter of a few fluids are compared with measurements made with a WITec Raman imaging microscope. For the WITec spectrometer measurements, the fluids were placed in an small open container, there was nothing between the fluid and the microscope. The integration time was set to 1 second and the number of accumulations was 100. For the Andor spectrometer measurements (home-built Raman), a small container was filled with the fluid and placed under the objective. The integration time was 0.97 s and the number of accumulation was also 100. Spectra of PAO 150, polybutene ($M_n = 1300 Da$) and PAO 150 + 10 wt% polybutene ($M_n = 1300 Da$) were acquired by both the WITec spectrometer and the Andor spectrometer and are given in figure 5.6. In the range of wavenumbers of interest, $700 cm^{-1}$ to $1500 cm^{-1}$, the spectra overlap very well, confirming that the home-built setup using the Andor spectrometer gives satisfactory results. It can be noted that under $500 cm^{-1}$, there are deviations between the spectra, mainly attributed to a difference in the baseline correction.

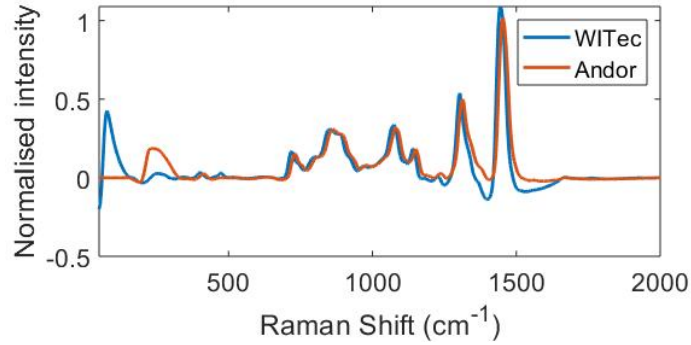
To confirm that spectra acquired at different positions of the contact can be compared to one another, Raman spectroscopy was done with PAO 150. The spectra are shown in figure 5.7. The reference is done under static conditions, a drop of fluid on a glass slide is positioned directly under the microscope. The three other spectra are acquired at the inlet ($400 \mu m$ upstream), in the contact, and at the outlet ($400 \mu m$ downstream), in a ball-on-disc contact running under pure rolling conditions. The four graphs are normalised using the peak at $1453 cm^{-1}$ (as this peak is common to PAO and polybutene, see table 5.4). The graphs overlap well, no shift of peaks occur between the reference and the spectra from the different positions in the running contact. This supports the use of this technique to perform chemical analysis across the contact. Hence, a change of intensity or wavenumber between spectra captures a real change in the fluid. It can be noted that in the three graphs corresponding to the running contact, three extra peaks appear between $400 cm^{-1}$ and $800 cm^{-1}$. They originate from the sapphire disc (see section 5.3.7). Their intensities depends on the position across the contact as the film thickness is lower in the contact than outside the contact. The intensity from the light scattered by the sapphire disc is relatively higher when the film is thin, so a thinner film in the contact leads to relatively higher sapphire peaks.



(a) PAO 150



(b) Polybutene ($M_n = 1300 \text{ Da}$)



(c) PAO 150 + 10 wt% polybutene ($M_n = 1300 \text{ Da}$)

Figure 5.6: Comparison between Raman spectra acquired with a WITec Raman imaging microscope (in blue) and the home-built Raman setup (Andor, in red), after baseline correction and normalisation

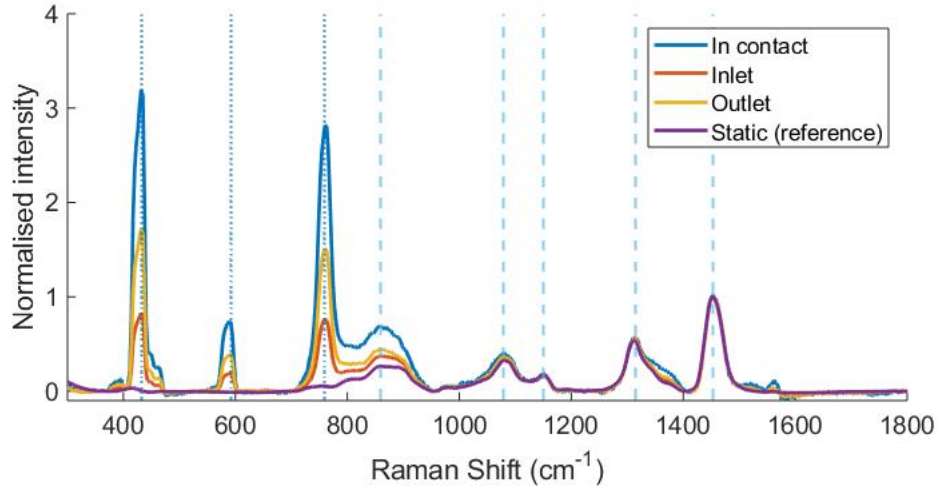


Figure 5.7: Raman spectra of PAO 150. The reference is acquired under static conditions (droplet on a glass slide). Comparison between the inlet ($-400\ \mu m$), the contact and the outlet ($+400\ \mu m$), in pure rolling, $T = 15\ ^\circ C$, $U_e = 0.3\ m/s$, $P_{mean} = 424\ MPa$.

5.3.4 Size of polymer molecules in polymer solutions

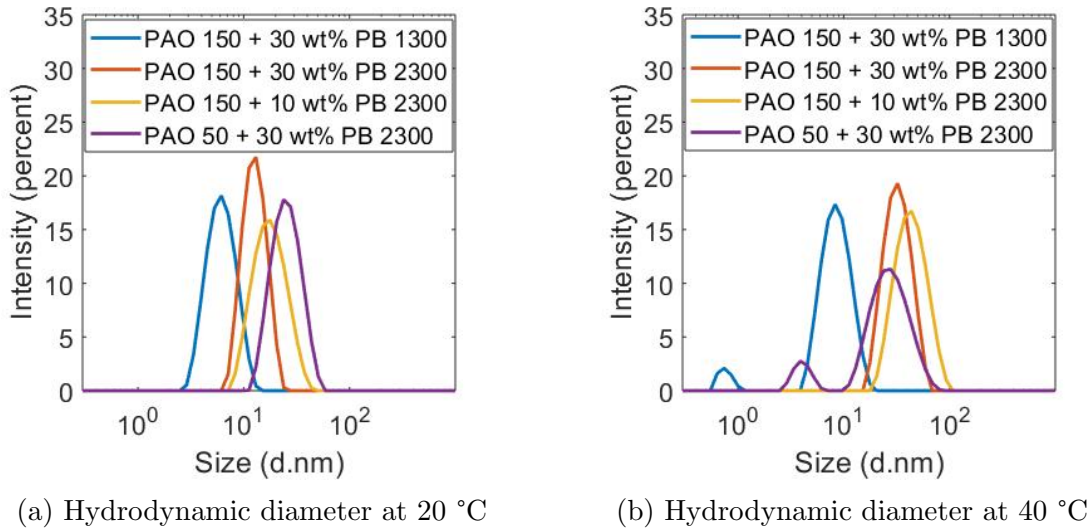


Figure 5.8: Size of polymer molecules measured by dynamic light scattering

It is critical to know the size of the polymer molecules, so that it can be compared to the film thickness of the contact. Molecules much smaller in size than the film thickness are expected to flow more easily into the contact than those which are in the range of the film thickness. The hydrodynamic diameter of the polymer molecules in the polymer solutions was measured by dynamic light scattering using a Zetasizer Pro (Malvern Panalytical). For both polybutenes, $M_n = 1300\ Da$ and $M_n = 2300\ Da$, and regardless of the solvent (PAO 50 and PAO 150), the hydrodynamic diameter is measured between 5 and 20 nm

at 20 °C, up to 50 nm at 40 °C. Distributions of the polymer size are given in figure 5.8. As expected, PB 1300 is smaller than PB 2300.

5.3.5 Shear-thinning behaviour

The viscosity at low shear rate was measured with the Stabinger viscometer, and at mid- and high-shear rate with the USV rig (PCS Instruments). More details on the shear thinning characterisation can be found in section 3.3. Due to the high viscosity of PAO 50, PAO 150, and of the polymer solutions, the viscosity under shear could be measured only at 100 °C and at low and mid-shear rates, below $3 \times 10^5 \text{ s}^{-1}$. Only for PAO 50 the viscosity could be measured up to $2 \times 10^6 \text{ s}^{-1}$, but above this shear rate the USV rig was reaching its maximum torque. Figure 5.9 shows the flow curves obtained. PAO 50 has a constant viscosity with increasing shear rates, it does not shear thin in this range of shear rates. However, when polybutene is added in PAO 50, there is shear-thinning as the mid-shear viscosity is lower than the low-shear viscosity. The drop in viscosity is slightly more substantial for the polybutene with the higher molecular weight (PAO 50 + 30 wt% PB 2300), even though this solution has a lower concentration of polybutene than PAO 50 + 50 wt% PB 1300. Neat PAO 150 already shear thins at the mid-shear rates, and so do all the polymer solutions made with PAO 150.

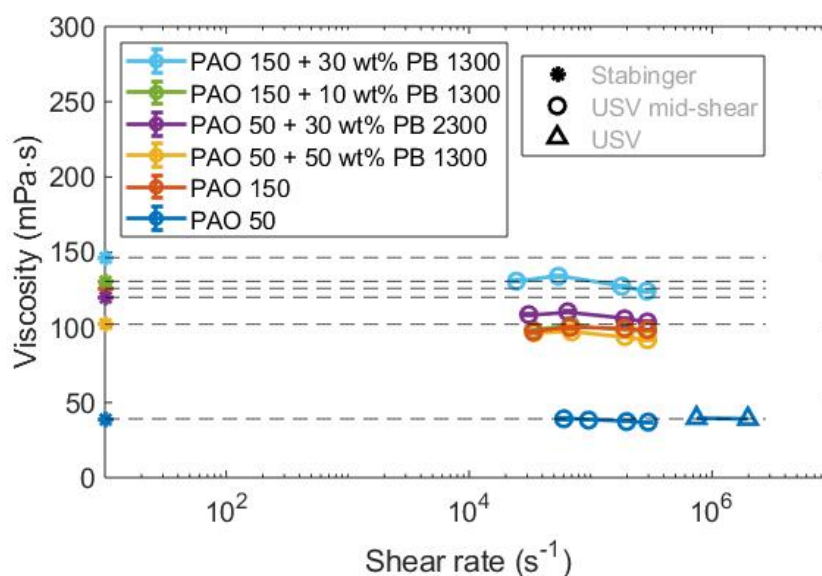


Figure 5.9: Viscosity as a function of shear rate for PAO 50, PAO 150, and the polymer solutions, at 100 °C. Different symbols are used for the data points from the low-shear Stabinger viscometer (stars), the mid-shear USV (circles) and high-shear USV (triangles). The horizontal lines represent the low-shear viscosity values. Green data points (PAO 150 + 10 wt% PB 1300) are overlapped by PAO 150 in red.

5.3.6 Experimental measurements of the film thickness of polymer solutions

The film thickness of the polymer solutions was measured using an EHD2 rig (PCS Instruments) at 25 °C, 40 °C, 60 °C and 80 °C, under pure rolling conditions. The specimens were a steel ball and a glass disc. The mean pressure in the contact was 350 MPa (load of 20 N). More details on film thickness measurements using interferometry can be found in section 3.1. The film thickness of all six polymer solutions and PAO 150 and PAO 50 at 40 °C are plotted in figure 5.10. PAO 150, PAO 50, and blends with PB $M_n = 1300$ Da give straight lines with gradients in the range 0.61 to 0.69 nm/(m/s). For the blends with PB $M_n = 2300$ Da, the film thickness flattens at high speeds, from 0.4 m/s for PAO 50 + 30wt% PB $M_n = 2300$ Da and from 0.3 m/s for PAO 150 + 30wt% PB $M_n = 2300$ Da. It can be noticed that PAO 150 + 30wt% PB $M_n = 2300$ Da also flattens at lower speeds, giving a thicker film than expected under 5 mm/s.

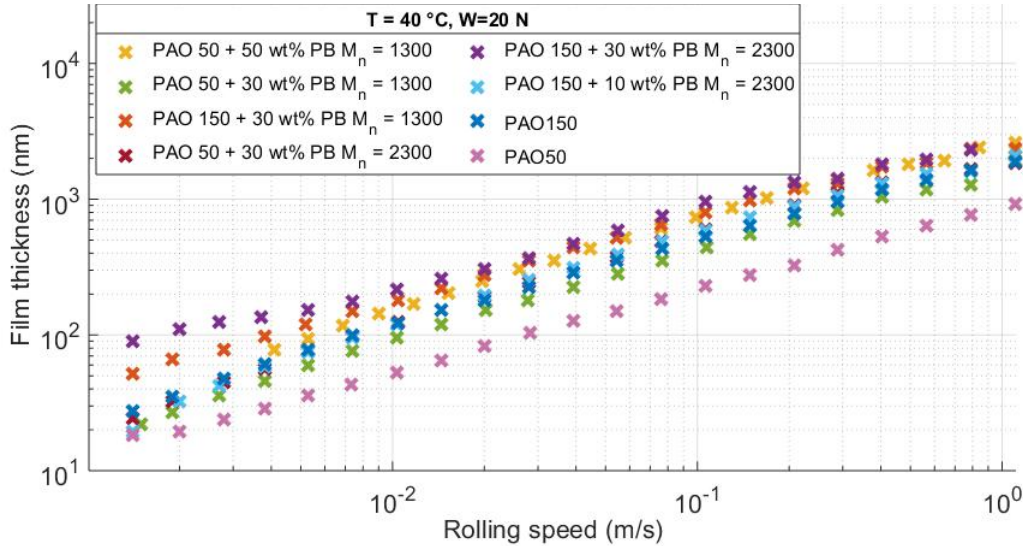


Figure 5.10: Film thickness of polymer solutions and neat PAO 150 and PAO 50, pure rolling (ball driven), 40 °C

The film thickness is driven by the inlet viscosity. In order to better visualise the link between these two parameters, the film thickness against the low shear viscosity of the fluids is plotted in figure 5.11. Solutions which have a similar viscosity have a different film thickness: PAO 50 + 50 wt% polybutene ($M_n = 1300$ Da) and PAO 50 + 30 wt% polybutene ($M_n = 2300$ Da) have the same viscosity, but the former has a higher film thicknesses (respectively blue and red data points overlapping at 1.65 Pa·s in figure 5.11). Polybutene ($M_n = 1300$ Da) is more effective in this case as it gives a higher film thickness. PAO 50 does not shear thin so the difference in film thickness might be attributed to more shear-thinning from PB 2300 than PB 1300. Since these solutions

have different solvents (and PAO 50 does not shear thin but PAO 150 does) and different polymers at different concentrations, no conclusion can be made on the influence of the solvent or of the polymer molecular weight. As expected, the film thickness increases with speed for all solutions.

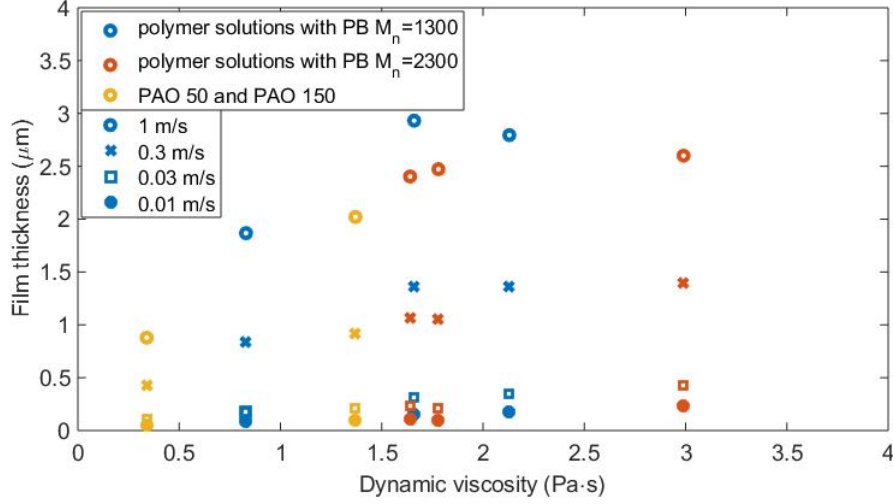


Figure 5.11: Film thickness at 4 different entrainment speeds, against viscosity ($T=40\text{ }^{\circ}\text{C}$)

Figure 5.12 gives two examples of the impact of temperature on film thickness. The behaviour of the film thickness does not change with increasing temperature, all the curves follow a similar linear trend. These results are for a glass-steel contact, while the Raman experiments are done with a sapphire-steel contact. To account for the differences in elastic modulus and contact pressure, the film thickness in the Raman experiment is corrected using the Chittenden and Dowson [172] equation

$$h_c \propto W^{-0.073} E^{*-0.117} \quad (5.1)$$

where h_c is the central film thickness, W the load and E^* is the reduced elastic modulus. More details on this model were given in section 2.9.1.

The effect of load on film thickness is shown in figure 5.13. In figure 5.13a, the film thickness of PAO 50 measured with the EHD2 is plotted. These raw values are then corrected to match the experimental conditions of the Raman spectroscopy experiment and reported in red in the figure. The corrected values are very slightly lower but the difference is negligible. Figure 5.13b is the film thickness of PAO 50 + 50 wt% polybutene ($M_n = 2300\text{ Da}$) at two loads, 10 N and 20 N (mean contact pressure of 280 MPa and 350 MPa, respectively). There is no noticeable difference between the two load conditions. These observations are in accordance with theoretical models, as the film thickness is proportional to the load with an exponent of -0.073 in equation (5.1), meaning that a small variation in the load has a negligible impact on the film thickness.

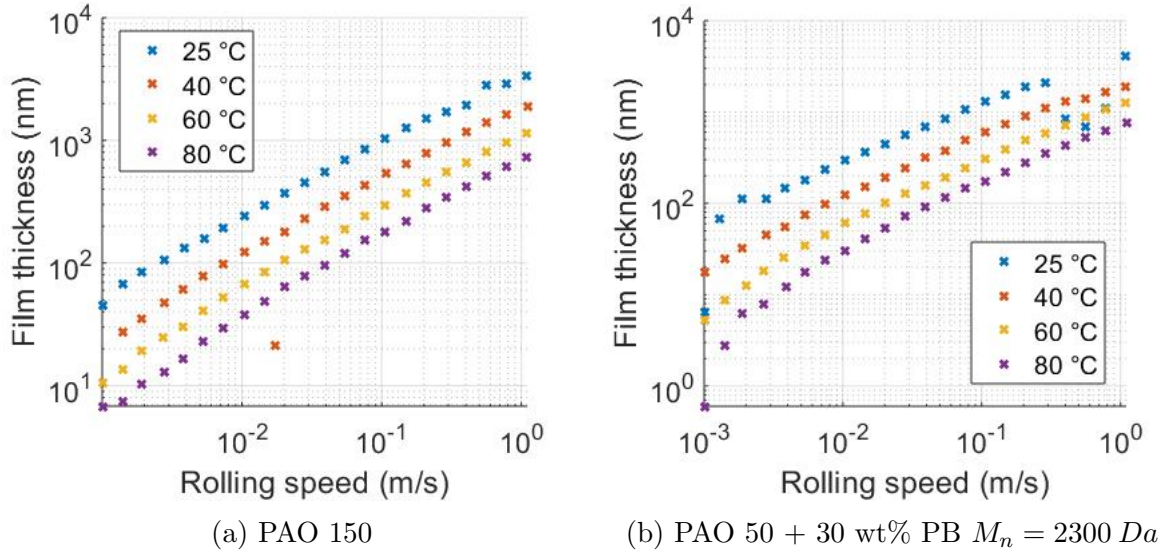
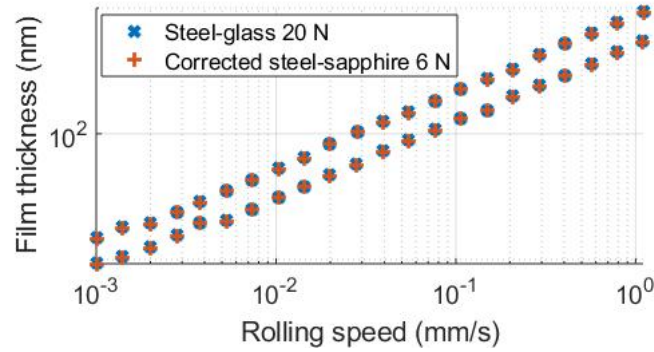
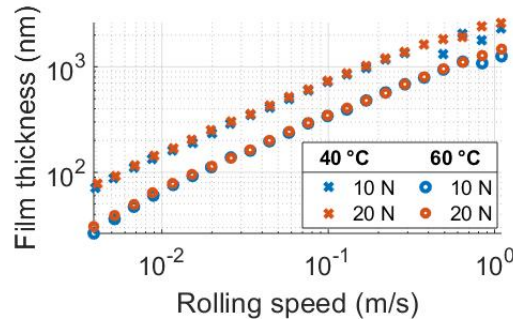


Figure 5.12: Effect of temperature on film thickness



(a) PAO 50, comparison between raw data (steel ball against glass disc, 20 N) and values after correction using equation 7.8 (steel ball against sapphire disc, 6 N). Temperatures are 40 °C and 60 °C.



(b) Effect of load on film thickness, PAO 50 + 50 wt% PB $M_n = 1300 Da$

Figure 5.13: Effect of load and material on film thickness: experimental measures and correction using Chittenden and Dowson.

5.3.7 Performing chemical analysis in a tribological contact

The peaks in the Raman spectra correspond to the species or component of the system. The polymer (polybutene), the solvent (PAO 50 or PAO 150) and the sapphire disc are identified using the Raman spectra of the neat fluids under static conditions (drop of fluid on a glass slide under the objective). These peaks are listed in table 5.4 and shown in figure 5.14. As some peaks are weak and other are overlapping, only a few are selected for the analysis, two for the polymer and two for the oil. They are in bold and red in table 5.4 and highlighted by red arrows in figure 5.14.

Table 5.4: Raman spectroscopy: polybutene, PAO and sapphire peaks (in cm^{-1}). Peaks selected for the analysis are in red.

Species	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
Polybutene	729	861	934	992	1161	1236	1354	1398	1451
PAO 50, PAO 150	859	1079	1150	1314	1453				
Sapphire	432	591.6	760						

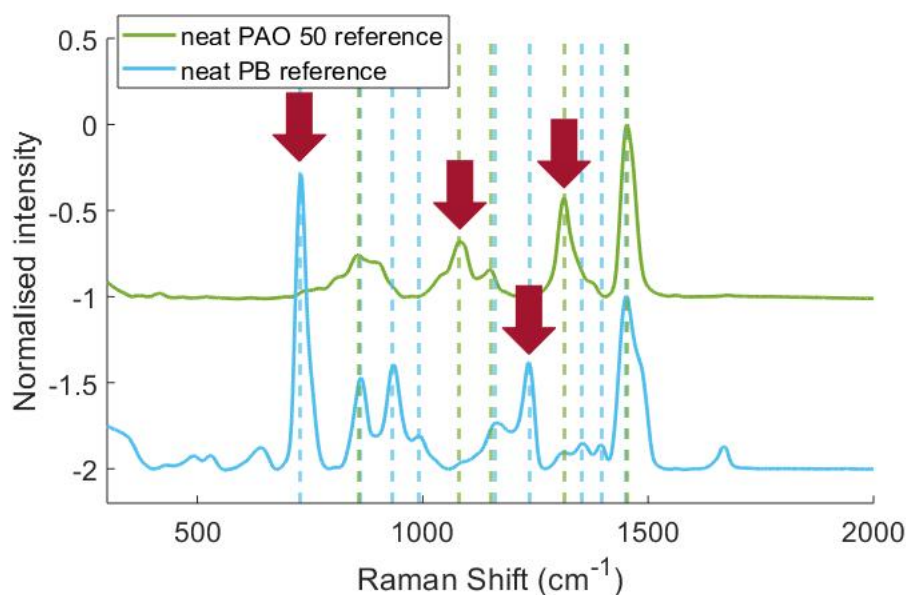
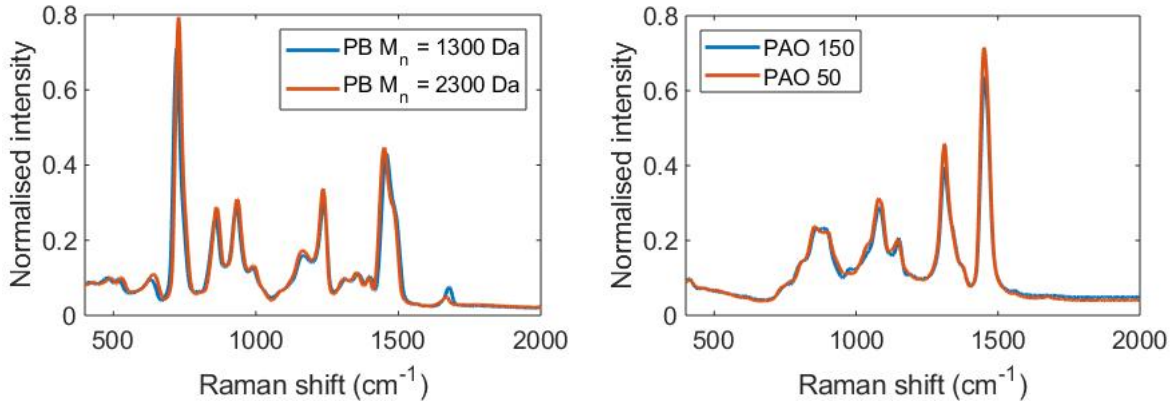


Figure 5.14: Raman spectra of neat polybutene and neat PAO 50 under static conditions. The peaks are identified with the vertical lines of corresponding colours. Red arrows highlight the peaks selected for the analysis.

It should be noted that the two polybutenes have similar Raman spectra, their peaks are at the same wavenumbers, and the same is observed for PAO 50 and PAO 150, with no differences in the position of their peaks. The spectra of both neat polybutenes can be seen in figure 5.15a, and in figure 5.15b for PAO 50 and PAO 150.



(a) Raman spectra of the two neat polybutenes, $M_n = 1300 \text{ Da}$ and $M_n = 2300 \text{ Da}$ (b) Raman spectra of PAO 50 and PAO 150

Figure 5.15: Raman spectra of the neat fluids, Andor spectrometer

Detecting peaks corresponding to the polymer molecules in a Raman spectrum acquired in the contact provides information on the composition of the polymer solution. The presence of peaks confirm that polymer molecules do enter the tribological contact. This is illustrated in figure 5.16 where the polymer is detected in the contact. The reference spectra are acquired under static conditions (fluids in small container under the objective). For the acquisition of the spectrum of the polymer solution in the contact, the entrainment speed was 1 m/s, in pure rolling, and the maximum pressure was 424 MPa. The peak at 1236 cm^{-1} is a peak for the polymer but not for PAO 50 so can be used to discriminate the two species. This specific peak appears clearly in the contact during rubbing (top spectrum in dark blue), meaning that in this case the polymer molecules are detected in the contact. The same apply to identify the solvent PAO 50 in the contact, for example by looking at the peak at 1079 cm^{-1} . The peak at 1079 cm^{-1} is specific for PAO 50 as it does not appear in the spectrum of polybutene.

Raman spectroscopy can be used to track the concentration of species spatially in the contact. Using absolute values of the intensity for comparisons is not possible in this experiment, as the intensity varies with laser alignment, focus, and thickness of the film at the point of acquisition. However, the ratio of polymer peaks and solvent peaks can give quantitative information on polymer concentration. A change in the ratio between a polymer peak and a solvent peak indicates a change of polymer concentration.

After acquisition, the Raman spectra need post-processing to be analysed and compared in a consistent manner. The first step is to perform a baseline correction. For all the spectra, the same data points are used for the baseline correction, as a different baseline correction would affect the intensity values, and also the ratio between peaks intensities. This would make the comparison of the polymer concentration at various

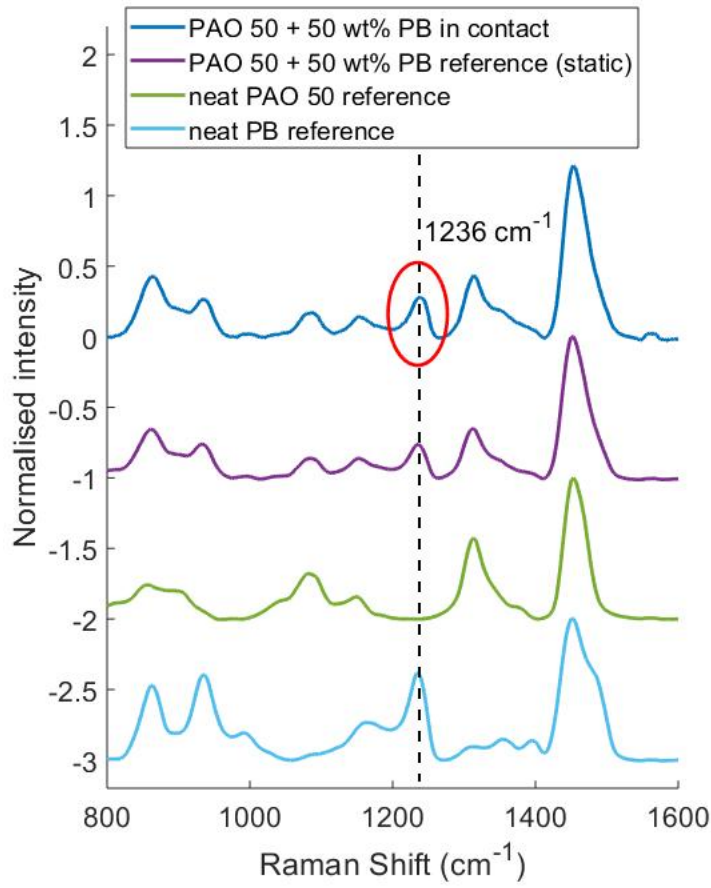


Figure 5.16: Raman spectra for neat polybutene, neat PAO 50 and a blend of PAO 50 + 50 wt% polybutene . The three spectra at the bottom are acquired under static conditions. The spectrum at the top for PAO 50 + 50 wt% polybutene is acquired in the contact, under pure rolling conditions, at $T = 26\text{ }^{\circ}\text{C}$, $U_e = 1\text{ m/s}$, $P_{mean} = 424\text{ MPa}$. A peak corresponding to the polymer molecules is clearly visible in the contact (red circle).

locations based on the relative intensities of polymer peaks impossible. Figure 5.17 shows a Raman spectrum before and after the baseline correction. The second step is the normalisation of the spectra, for easier visualisation and comparison. The first sapphire peak at 432 cm^{-1} is used for the normalisation of the Raman spectra acquired in the contact. As both the excitation light and the Raman scattered light go through the sapphire disc during the experiment, the spectra are polluted with three peaks coming from the sapphire, at 432 cm^{-1} , 592 cm^{-1} and 760 cm^{-1} as seen in figure 5.18. Only the last peak overlaps slightly with a polymer peak, but deconvolution shows that they are far enough to each other not to interfere (see section 5.3.8). When the sapphire peaks are not present in the Raman spectrum (for instance when the measurement is done under static conditions - without the sapphire disc), the peak at 1453 cm^{-1} is used for normalisation.

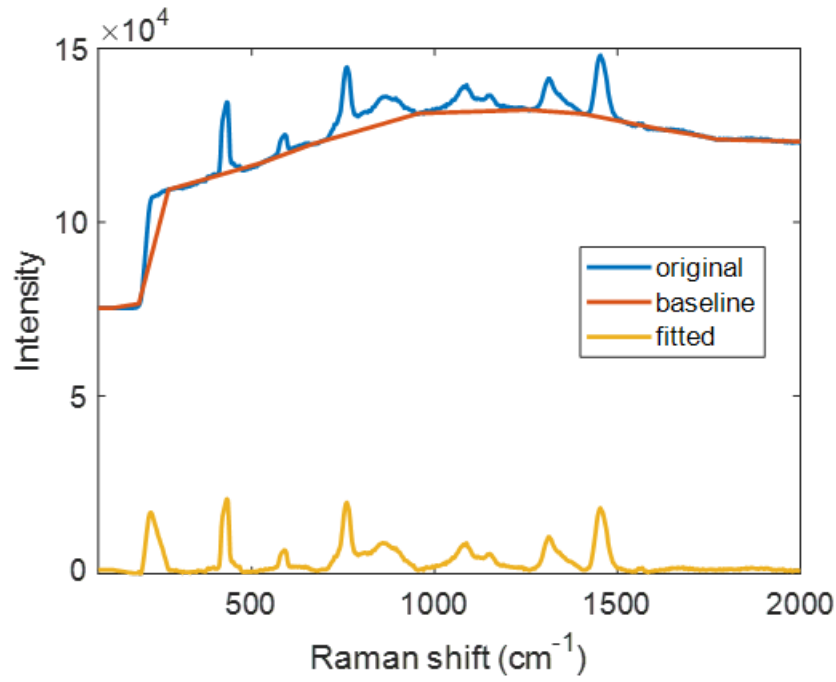


Figure 5.17: Raman spectrum before baseline correction in blue. The baseline is in red, and the fitted final Raman spectrum used for further analysis in yellow.

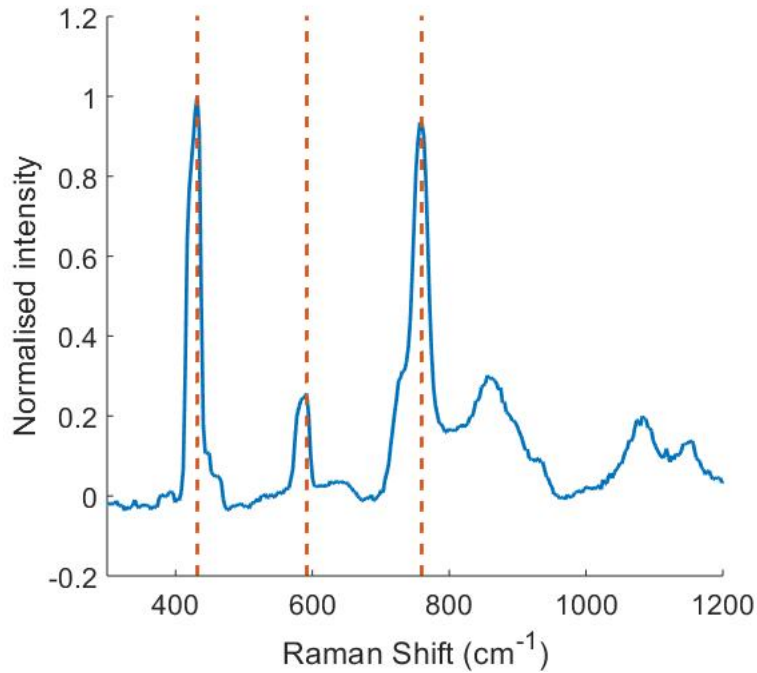


Figure 5.18: Raman spectrum of PAO 150 + 30 wt% PB (M_n 2300 Da) in pure rolling, $T = 25\text{ }^\circ\text{C}$, $U_e = 0.3\text{ m/s}$, $P_{mean} = 424\text{ MPa}$. The three sapphire peaks are identified with the vertical lines.

5.3.8 Deconvolution of two overlapping peaks

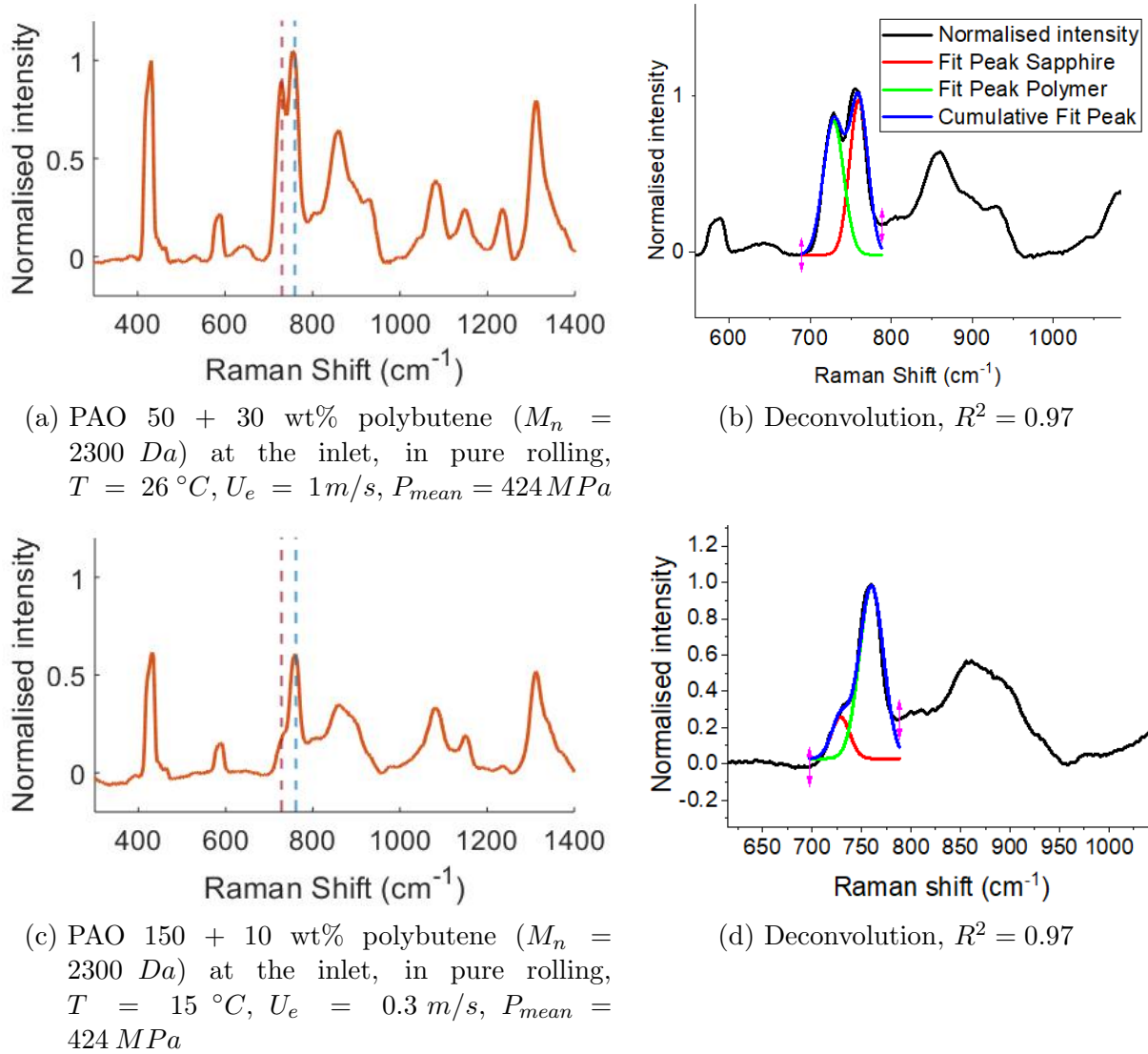


Figure 5.19: (a) and (c): Raman spectra highlighting a polymer peak and a sapphire peak close to each other. The red vertical line represents the polymer peak ($729 cm^{-1}$), and the blue vertical line the sapphire peak ($760 cm^{-1}$). (b) and (d): Respective deconvolution with a Gaussian fit of the two peaks.

The first polymer peak chosen for the analysis, at $729 cm^{-1}$, is close to a sapphire peak, at $760 cm^{-1}$, as shown in figures 5.19a and 5.19c. Consequently, the intensity coming from the sapphire might impact the intensity value of the polymer peak. A deconvolution is performed to assess the impact of this sapphire peak on the polymer peak. The deconvolution is done with a Gaussian fit where the Raman shift values of the two peaks are fixed to $729 cm^{-1}$ and $760 cm^{-1}$. The intensities of these two peaks before and after the deconvolution are listed in table 5.5. The change in the intensity of the peaks is very

small after the deconvolution, consequently it is decided not to perform any deconvolution when using the polymer peak at 729 cm^{-1} in the analysis.

Table 5.5: Comparison of the intensities at the peaks before and after deconvolution

	PAO 50 + 30 wt% polybutene see figure 5.19b		PAO 150 + 10 wt% polybutene see figure 5.19d	
	$I_{polymer\ 729\text{ cm}^{-1}}$	$I_{sapphire\ 760\text{ cm}^{-1}}$	$I_{polymer\ 729\text{ cm}^{-1}}$	$I_{sapphire\ 760\text{ cm}^{-1}}$
Before deconvolution	0.89	1.00	0.29	1.00
After deconvolution	0.84	0.98	0.26	0.98

5.3.9 Limitation on film thickness

At low speeds and high temperatures, the film thickness decreases and the Raman response of the fluid in the contact is too low to capture a signal. The minimum film thickness giving a sufficient intensity is estimated to be around $1.5\text{ }\mu\text{m}$. Figure 5.20 shows the normalised Raman spectra of PAO 150 + 30 wt% PB ($M_n = 2300\text{ Da}$) at different temperatures. At the highest temperature $58\text{ }^\circ\text{C}$, the central film thickness is $0.9\text{ }\mu\text{m}$, and at $40\text{ }^\circ\text{C}$ the central film thickness is $1.4\text{ }\mu\text{m}$. The signal from the solution at these two temperatures is weak and hardly distinguishable. This means that calculating and comparing intensity ratios using these spectra has to be done with care.

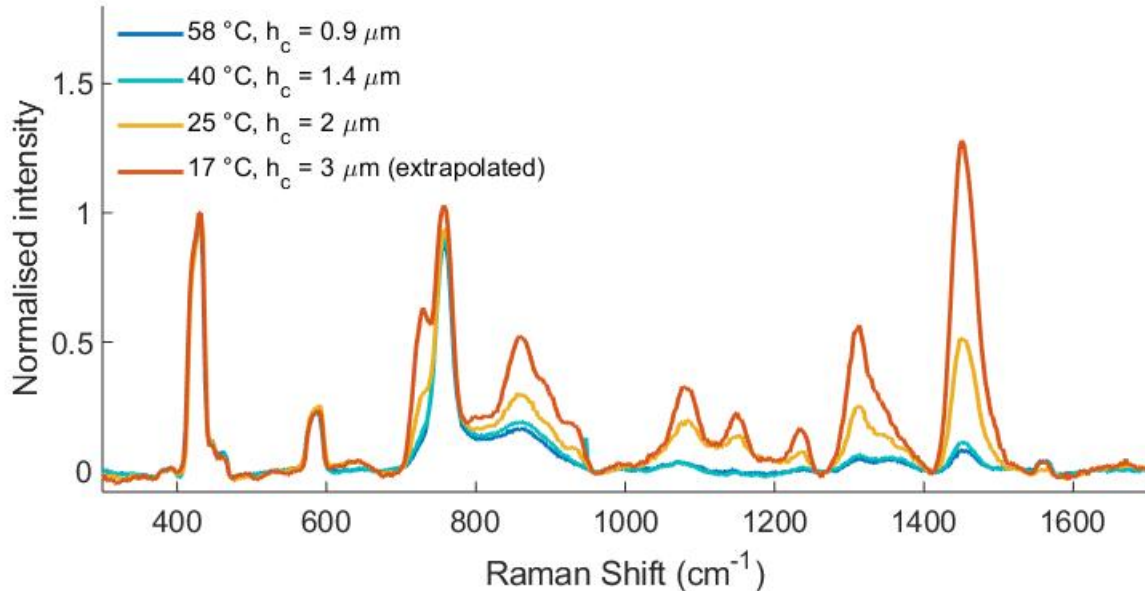


Figure 5.20: Raman spectra of PAO 150 + 30 wt% PB ($M_n = 2300\text{ Da}$) at different temperatures, at the centre of the contact, $U_e = 0.3\text{ m/s}$, $P_{mean} = 424\text{ MPa}$, $SRR = 0\%$

5.4 Results

5.4.1 Effect of concentration

To assess if the ratio between the intensity of a polymer peak and the intensity of a PAO peak in a Raman spectrum gives a quantitative measure of the polymer concentration, measurements were done using polymer solutions with different concentrations.

Raman spectra were first acquired under static conditions, both the ball and the disc were not in motion. The ball was not loaded against the disc, hence there was a thick meniscus of solution between the two surfaces giving a high-intensity Raman scatter. The ratios of the four peaks of interest from Raman spectra of the six polymer solutions at different temperatures can be found in figure 5.21. There is a clear link between the value of a ratio and the polymer concentration. All the ratios for a concentration of 30 wt% overlap. There is no dependency on the solvent or the polymer molecular weight.

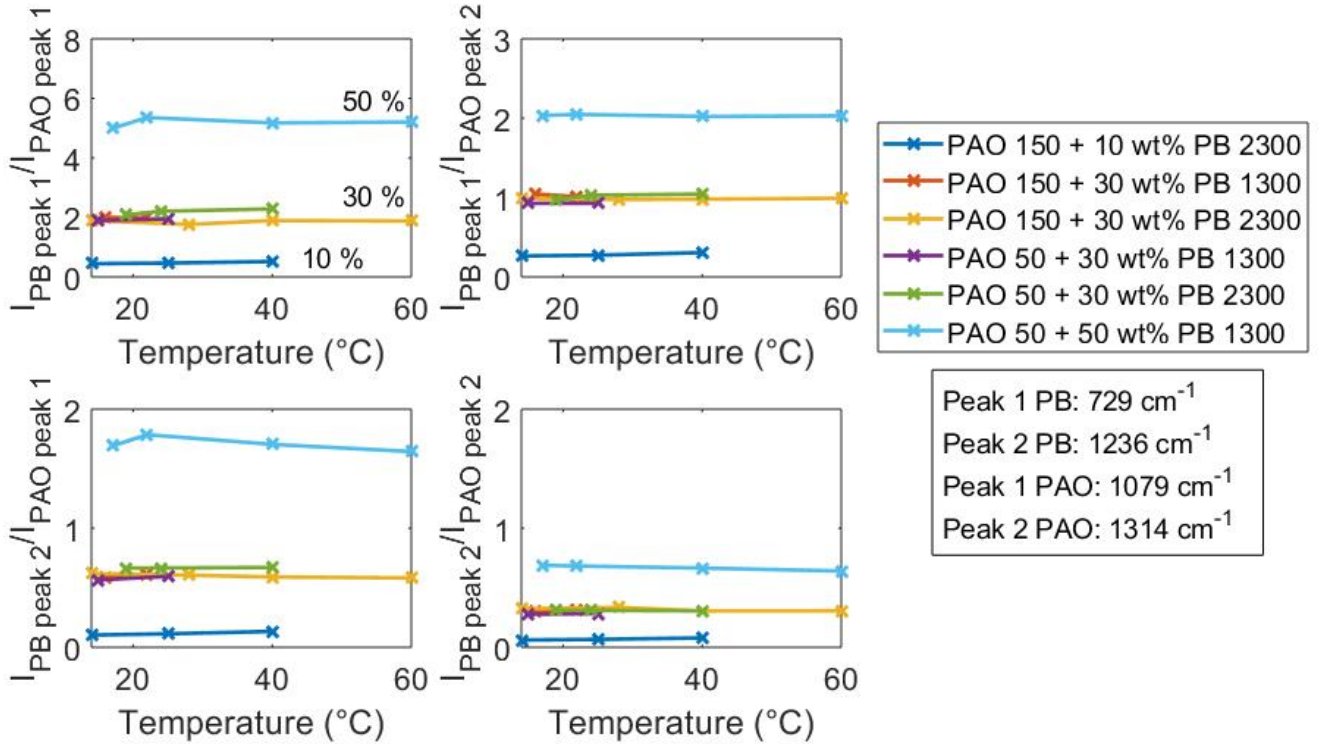
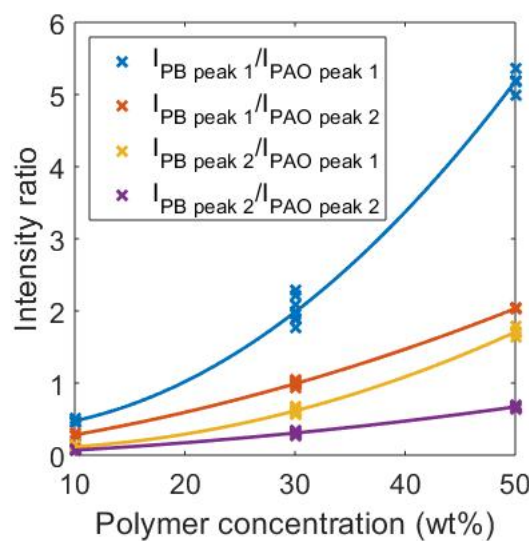


Figure 5.21: The four ratio of intensities $I_{PB \text{ peak}} / I_{PAO \text{ peak}}$ against temperature, for the six polymer solutions under static conditions.

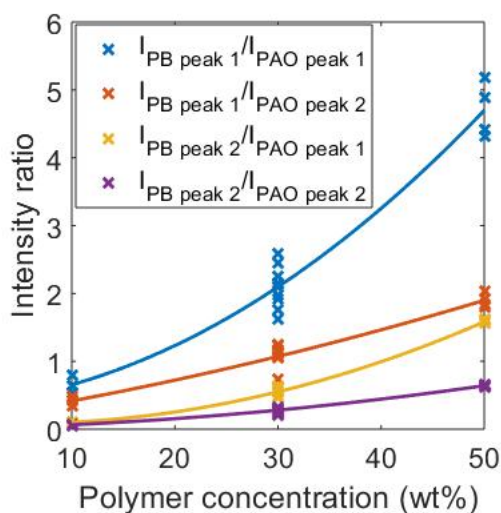
The analysis was extended to the contact under pure rolling conditions. For all the six polymer solutions, measurements were taken at the inlet and at the centre of the contact, with an entrainment speed U_e of 0.3 m/s and an average contact pressure P_{mean} of 424 MPa. Figure 5.22 shows the four ratios of interest against polymer concentration in the three cases: the static case (simple case, high intensity of the Raman scatter),

under pure rolling at the inlet (good intensity) and in the contact (lowest intensity). The intensity was lower in the contact in this case due to a lower film thickness than under static conditions where no pressure was applied, leading to a wider spread of ratio values. However, the trend was the same for the three cases: the ratio is directly related to the concentration of the polymer and does not depend on the solvent or polymer molecular weight.

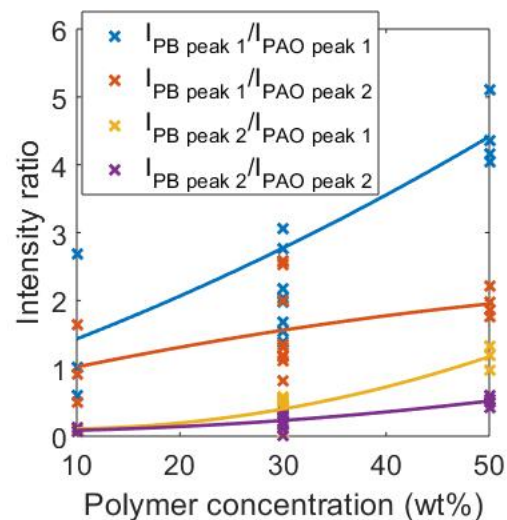
This shows that the developed method can give quantifiable information on polymer concentration.



(a) Static conditions



(b) Inlet, pure rolling
 $U_e = 0.3 \text{ m/s}$, $P_{mean} = 424 \text{ MPa}$



(c) In contact, pure rolling
 $U_e = 0.3 \text{ m/s}$, $P_{mean} = 424 \text{ MPa}$

Figure 5.22: Ratio of intensities between polymer peaks and PAO peaks in the Raman spectrum against polymer concentration. Markers are experimental data points, lines are polynomial fits (order 2).

5.4.2 Do polymer molecules enter the tribological contact?

It can be assessed if the polymer molecules enter the contact by tracking the polymer concentration across the contact, ranging far from the inlet to the outlet.

With the fluid PAO 150 + 30 wt% polybutene ($M_n = 2300 Da$), a series of Raman measurements were performed at different positions along the contact. The normalised Raman spectrum at each position can be found in figure 5.23. The intensity is lower in the contact due to a lower film thickness of the fluid compared to outside of the contact. The intensity is also lower at the outlet, close to the contact, due to the cavitation in this region. For instance, the intensity at the outlet, 200 μm downstream from the contact, is 3 times lower than the intensity at the inlet, 400 μm upstream from the contact, and 2 times lower than the intensity at 200 μm upstream from the contact.

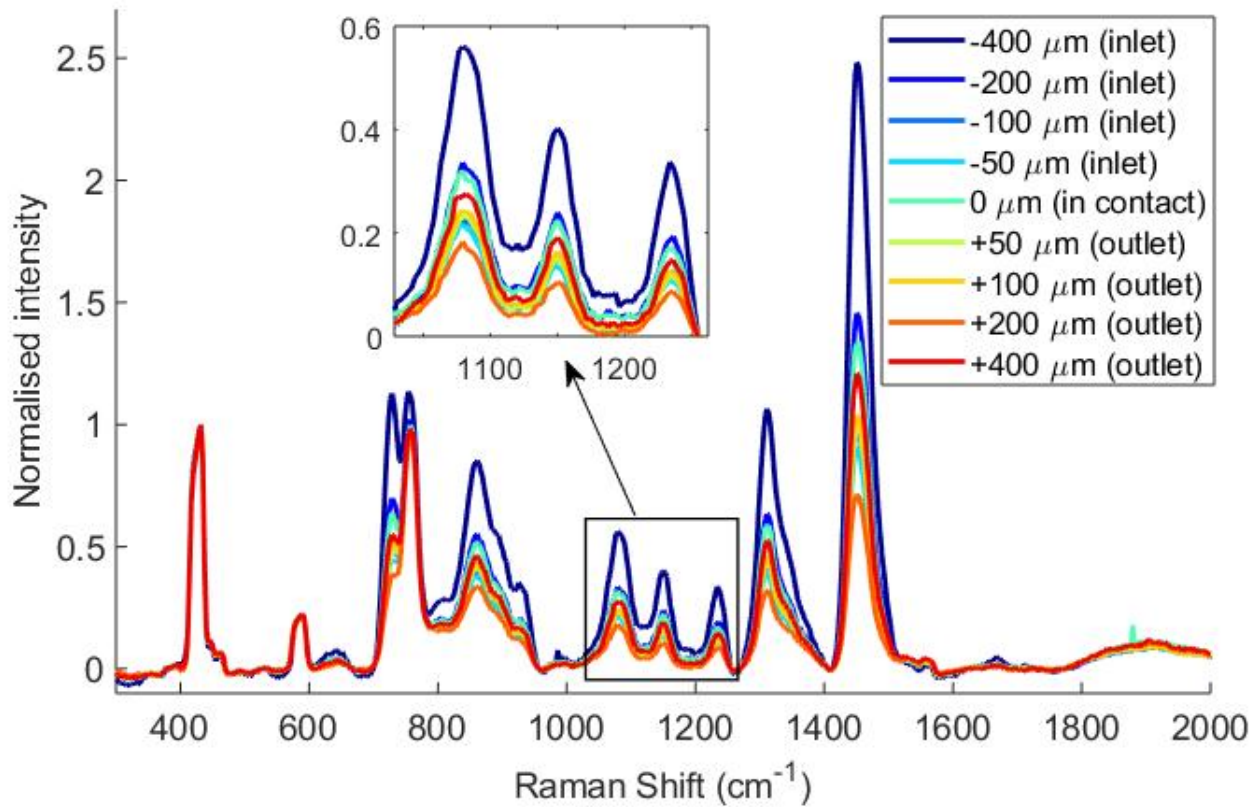


Figure 5.23: Normalised intensity at different positions from the inlet to the outlet, PAO 150 + 30 wt% polybutene ($M_n = 2300 Da$), pure sliding ($SRR = -200\%$), entrainment speed 0.3 m/s, 15 °C. Insert is a zoom-in for greater clarity.

The ratios between the intensity of polybutene peaks and the intensity of PAO 150 peaks were calculated from the spectra at each position and are reported in figure 5.24. The value of each ratio is fairly constant across the contact, there is no change between the polymer concentration at the inlet and in the contact. The results in figure 5.24 confirm that the polymer is not depleted nor accumulated at the inlet.

As the thickness of the film (in the range of $2\text{ }\mu\text{m}$) is much higher than the size of the polymer molecules, around 10 nm (see section 5.3.4), it was expected to find the same polymer concentration outside and inside the contact.

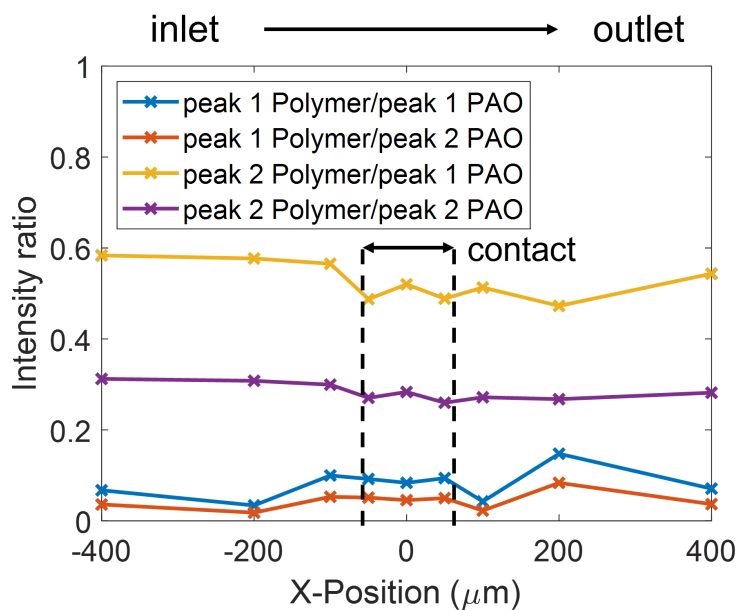


Figure 5.24: PAO 150 + 30 wt% polybutene ($M_n = 2300\text{ Da}$), pure sliding ($SRR = -200\%$), entrainment speed 0.3 m/s , $15\text{ }^\circ\text{C}$. The vertical dashed lines represent the diameter of the contact.

5.4.3 Effect of slide-roll ratio

The effect of slide-roll ratio is investigated for the solution PAO 150 + 30 wt% polybutene ($M_n = 2300\text{ Da}$). The four ratios between the intensities of the polymer peaks and oil peaks in the Raman spectra are reported in figure 5.25 at the inlet, in the contact and at the outlet. The ratios have the same value regardless of the sliding conditions or the position of interest. In this case, the polymer concentration does not change with slide-roll ratio. The data points at $SRR = +200\%$ are not reliable, as when the ball is static, the fluid is not entrained and the contact is insufficiently lubricated. These results show that the entrainment of polymer is not affected by slide-roll ratio.

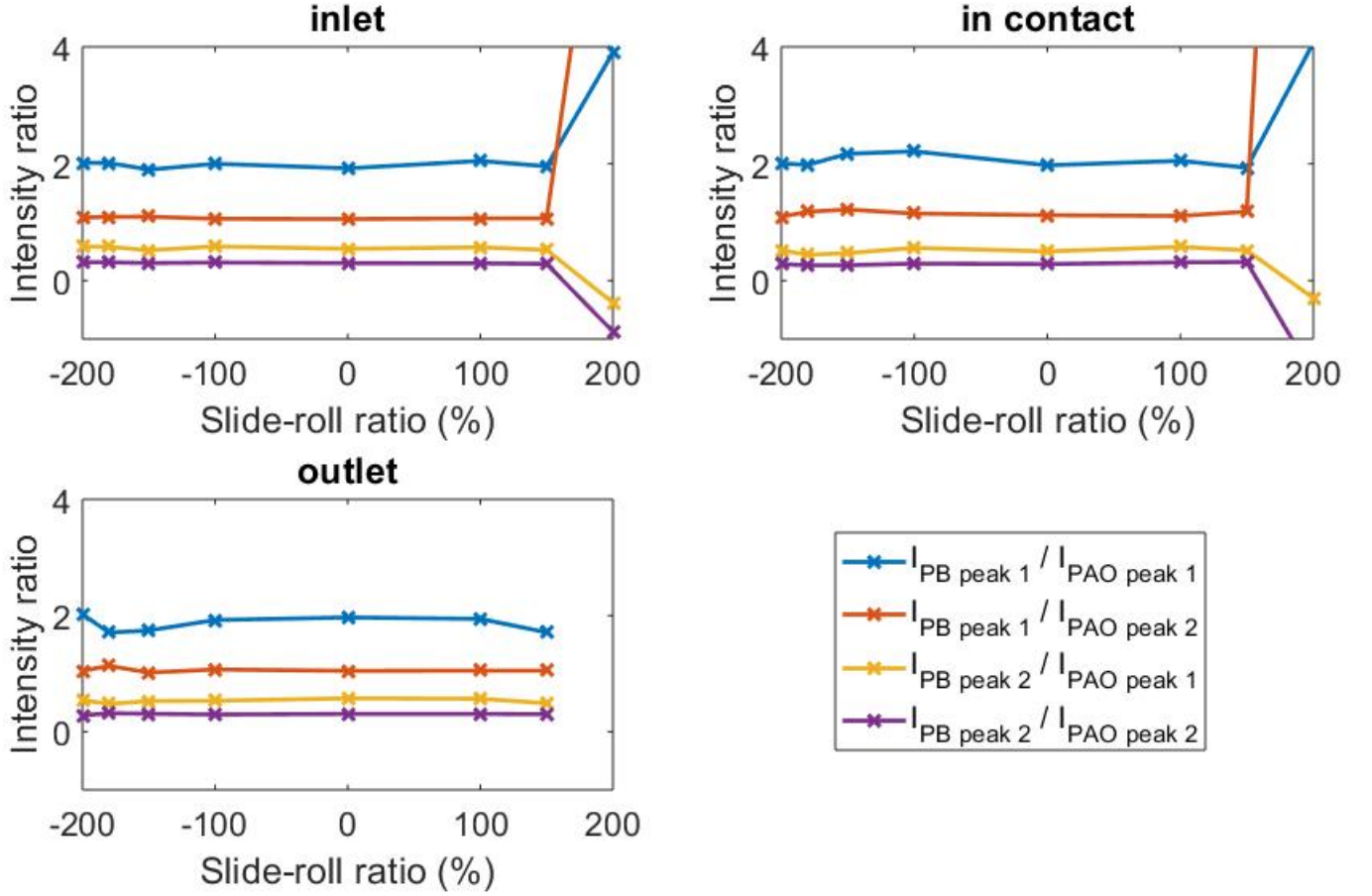


Figure 5.25: PAO 150 + 30 wt% PB ($M_n = 2300 \text{ Da}$), $T = 15 \text{ }^\circ\text{C}$ $U_e = 0.3 \text{ m/s}$, $P_{mean} = 424 \text{ MPa}$. SRR = -200 % is pure sliding with a stationary disc, SRR = +200 % is pure sliding with a stationary ball.

5.5 Conclusions

A novel *in situ* Raman spectroscopy technique was successfully implemented in a ball-on-disc contact in the elastohydrodynamic regime. Chemical analysis along the contact was performed and used to track polymer concentration at the inlet, in the contact and at the outlet. This work shows that Raman spectroscopy could be used as a technique to estimate the concentration of polymer solutions, provided that a calibration curve is obtained.

This work aimed at identifying the possible mechanisms driving the film thickness of polymer solutions, and assessing if the polymer molecules enter the contact. Results suggest that for the six polymer solutions investigated, the polymer molecules enter the contact. The ratios between the intensity of polymer peaks and solvent peaks were dependent on polymer concentration, but not on the position of the measurement (in the contact, at the inlet, or at the outlet). No depletion or aggregation were observed

at the inlet or in the contact. Consequently, a deviation of the film thickness from what is expected based on the low-shear viscosity does not originate from a change in the polymer concentration at the inlet. This supports inlet shear-thinning or shear-heating as the mechanisms for film thickness reduction. Viscosity measurements showed that the tested polymer solutions experience shear-thinning at medium and high shear rates.

It should be noted that the technique has some limitations. The main limitation is the good Raman intensity requires a minimum film thickness of about $1.5\ \mu\text{m}$ for PAO+PB systems. To meet this requirement, very viscous fluids were used. A high viscosity was achieved by using viscous base oils and a high concentration of polymers.

Raman spectroscopy can provide valuable information on local fluid composition. Future work should focus on improving the sensitivity of the technique to apply it to more realistic lubricants and conditions.

Chapter 6

Local viscosity measurements in a tribological contact in the elastohydrodynamic regime

In this chapter, the measurement of viscosity *in situ* in a ball-on-disc tribological contact is investigated. Two methods are presented, based on fluorescence lifetime spectroscopy and anisotropy. Preliminary results are outlined.

6.1 Measuring local viscosity *in situ* in an EHD contact

Techniques based on fluorescence anisotropy and fluorescence lifetime spectroscopy were developed by Wong's group at Imperial College London to measure *in situ* viscosity and its spatial variations in a ball-on-disc EHD contact, attaining viscosities up to 300 Pa·s, at pressures up to 1.2 GPa and shear rates up to 10^5 s^{-1} [140, 176].

The principles of fluorescence lifetime and anisotropy can be found in more details in section 3.4.

With fluorescence anisotropy, conventional fluorophores are used. It is thus relatively easy to find a dye compatible with a hydrophobic system. Dench [141] used Nile red to access viscosity maps of PAO 8 at different pressures using fluorescence anisotropy. Using this technique, the range of viscosity they could measure using Nile Red was limited to 0.0004 - 7.6 Pa·s.

Using fluorescence lifetime, Dench *et al. et al.* [140] accessed viscosities up to 300 Pa·s. However, they could only use hydrophilic systems due to limitations on the availability of dyes that are soluble in oil-based systems. Dyes used in fluorescence lifetime experiments were originally developed for biology or biophysics, where systems are typically aqueous

and with low viscosity. Another drawback of the technique is its high cost, mainly due to the cost of the femtosecond laser they used.

The aim of my work is to improve these two techniques and adapt them to new systems, oil-based and containing viscosity modifiers. First, the laser is replaced by a Light Emitting Diode (LED) in the fluorescence anisotropy setup. The femtosecond laser used by Dench *et al.* [141] was a class 4 laser. Class 4 is the highest and most dangerous class of lasers. A LED is safer than a laser and is also much more affordable, about 1500 times less expensive than the laser. Thanks to recent advances, emissions of LEDs now have a narrower distribution around their nominal wavelength, making them good candidates for fluorescence applications. The goal is to conduct the experiment in wide-field mode, *i.e.* capturing a full image of the contact in one measurement using a LED. So instead of 121 images to map the contact as in Dench *et al.* [141], only 1 image would be needed to obtain information from the whole contact with a LED. If successful, using a LED would not only have safety and cost benefits, but also improve the time resolution of the technique.

Using the fluorescence lifetime technique, a preliminary study is carried out using a new dye, Bodipy. The objective is to assess if this technique can be used to measure the viscosity of hydrophobic systems, to explore the limitations on the maximum viscosity and its applicability to multi-component fluids (polymer solutions).

6.2 Fluorescence anisotropy using a LED for *in situ* viscosity measurements

6.2.1 Materials and methods

This optical setup is based on the one developed previously by Dench *et al.* [141]. The tribological contact is a glass ball pressed against a glass disc, mounted on top of an inverted microscope. The speed of the ball and the disc is controlled by two motors, and the pressure in the contact by a dead weight on the ball. The disc is thin and transparent to provide optical access to the contact. The optical setup is presented in figure 6.1. The material chosen for the ball was also glass as steel was giving too much reflection. The excitation source is a 470 nm blue LED from Thorlabs. To remove the pattern of the light, a diffuser is placed after the LED, giving a Gaussian distribution to the illumination. The light is then collimated using two lenses and a telescope, and vertically polarised by a polariser. An objective focuses the light into the contact and captures the fluorescence light emitted by the dyed oil. Objectives with a magnification of x5 and x10 are used. The analyser, placed just before the camera, is held in a rotating mount so it can discriminate the light polarised vertically or horizontally. Both vertical and horizontal components are

needed for anisotropy measurements. Dench *et al.* [141] captured the two components of the polarisation simultaneously using two cameras. They had to use a corrective factor to take into account the difference in sensitivity between the two cameras. Having the polariser in a rotating mount enables horizontal and vertical measurements to be taken with the same camera, reducing greatly the difference in sensitivity between these two components and giving a more reliable resultant anisotropy. As the experiments are performed in a steady state, the acquisition of the vertical and horizontal components of the polarisation can be done one after the other. The emission light is collected by a Raptor EMCCD camera.

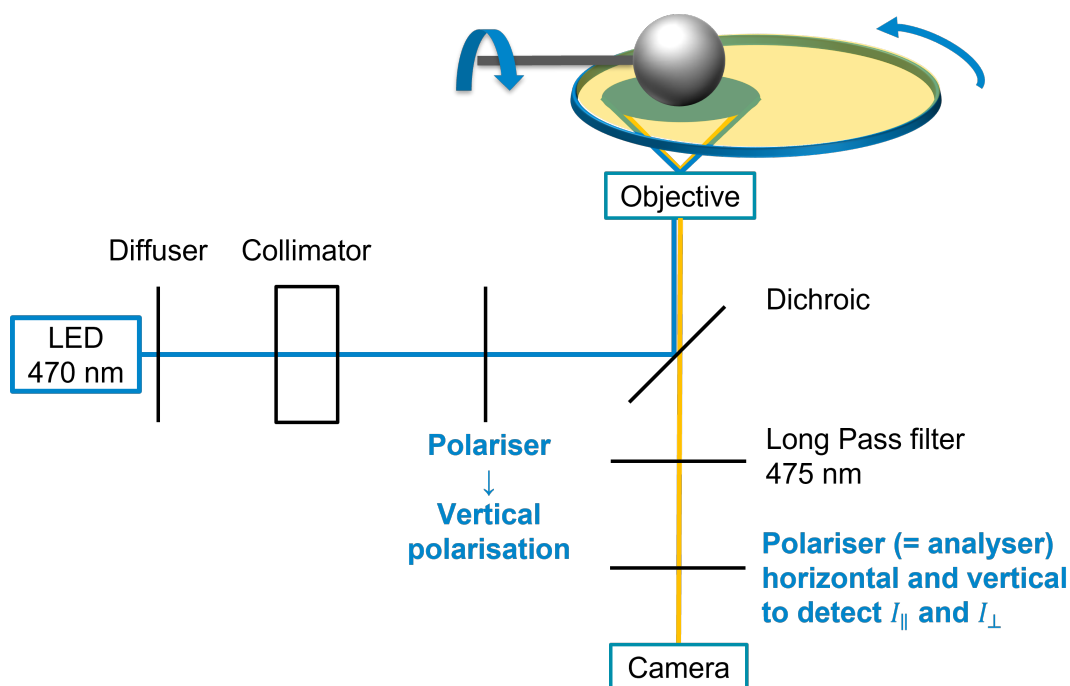


Figure 6.1: Fluorescence anisotropy optical setup

The test fluids are polyalphaolefin (PAO) of different viscosities from INEOS Oligomers (Durasyn) and ExxonMobil (SpectraSyn). Polybutene (PB) from INEOS Oligomers (Indopol H-300) was used as a viscosity modifier and blended with PAO 4 and PAO 8. For the calibration curve, toluene and isopropanol from Sigma Aldrich were also used to access lower viscosities. The dye used for all solutions was Nile Red, from Sigma Aldrich, at a concentration ranging between 0.2-0.4 mM. Nile red was dissolved using magnetic stirring at 80 °C for at least 1 hour. These solutions were then filtered with 1 μ m glass filters from VWR. The solutions and their viscosity measured with a Stabinger viscometer (Anton-Paar) are listed in table 6.1.

Table 6.1: Fluids used for fluorescence anisotropy and viscosity

Fluid	Viscosity at 22 °C (Pa.s)
Toluene	0.0006
Isopropanol	0.0022
Durasyn 164	0.0342
Durasyn 145	0.0514
SpectraSyn 4 (PAO 4)	0.0287
SpectraSyn 8 (PAO 8)	0.0902
SpectraSyn 40 (PAO 40)	1.0671
SpectraSyn 100 (PAO 100)	3.9266
PAO 4 + 11 wt% PB	0.0526
PAO 4 + 24 wt% PB	0.1225
PAO 8 + 9 wt% PB	0.1388
PAO 8 + 15 wt% PB	0.1909
PAO 8 + 22 wt% PB	0.2812

6.2.2 Anisotropy-viscosity calibration in bulk

The first calibration was done in bulk and static conditions, to verify that the anisotropy is a linear function of the logarithm of the viscosity as reminded below equation 3.4. This is particularly important for the solutions containing PB as the polymer might have an impact on the anisotropy-viscosity relationship.

$$r = A \ln \eta + B \quad (3.4)$$

A quartz cuvette filled with a solution was placed above the inverted microscope, in place of the EHD ball-on-disc element. Then 4 sets of 100 images were taken, with the polarisers oriented vertically or horizontally. The 100 images of each set were averaged, in order to reduce the noise. The anisotropy was then calculated using equation 6.1a, where I is the intensity after background correction (subtraction of dark image, acquired with LED turned off), the first subscript letter is the orientation of the polariser and the second is the orientation of the analyser (V is for vertical and H is for horizontal). G is a correction factor calculated using equation 6.1b.

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (6.1a)$$

$$G = \frac{I_{HV}}{I_{HH}} \quad (6.1b)$$

The resulting calibration curve is shown in figure 6.2, the x-axis is logarithmic. All PAO fluids and the low viscosity solvents align well. The polymer solutions also follow the same relationship, meaning that no specific calibration is needed for PB-containing fluids.

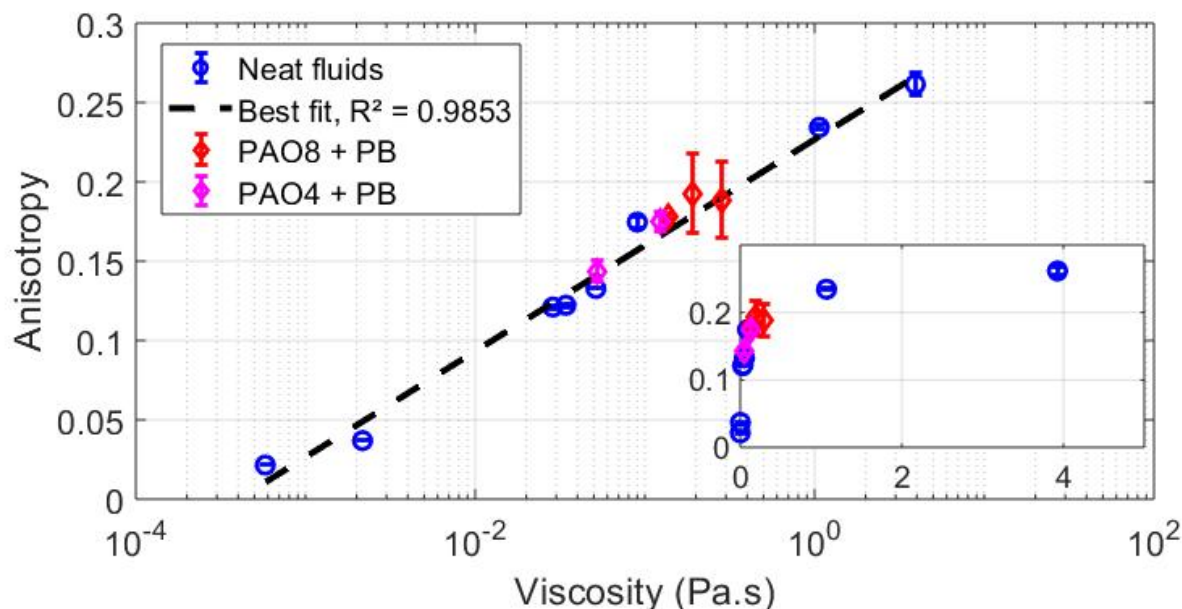
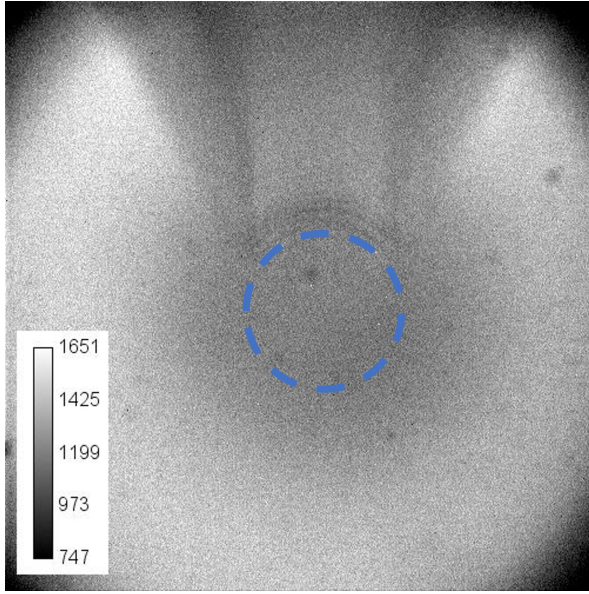


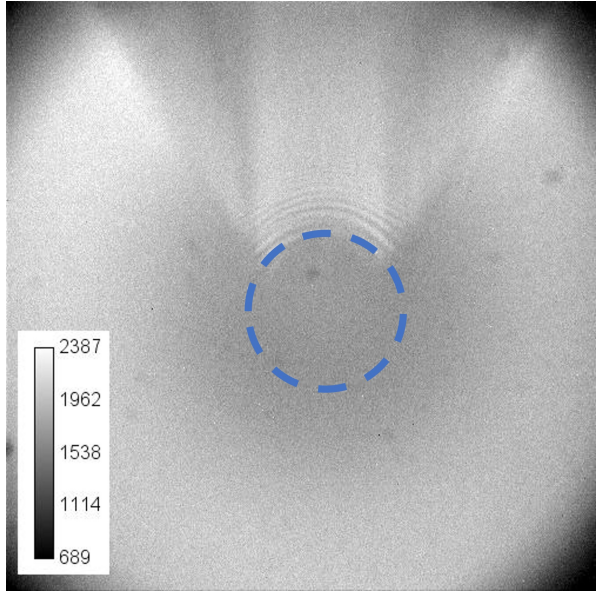
Figure 6.2: Calibration anisotropy-viscosity, error bars are standard deviations, dotted line is best fit. Dye is Nile Red. Polymer solutions are highlighted in red (PAO 8) and pink (PAO 4). Insert is linear plot.

6.2.3 Ball-on-disc EHD contact imaging

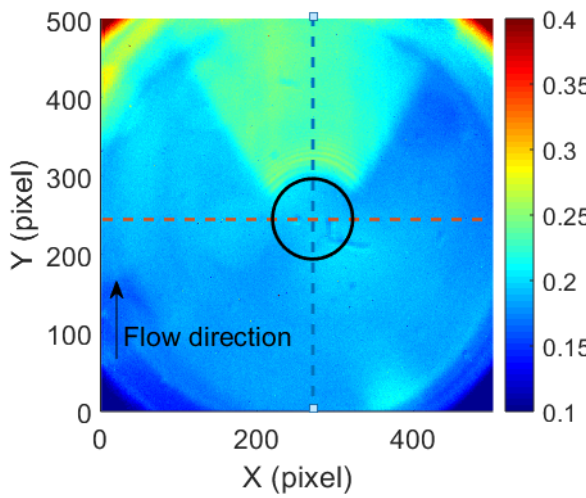
Images of the ball-on-disc contacts were acquired under different sliding and load conditions. Unfortunately, the technique failed to generate any usable data. While a clear difference in intensity could be seen between different configurations of the two polarisers (VH for vertical polariser and horizontal analyser, and VV for vertical analyser and vertical polariser), the distribution in the contact was homogeneous, no variation of intensity hence viscosity could be detected.



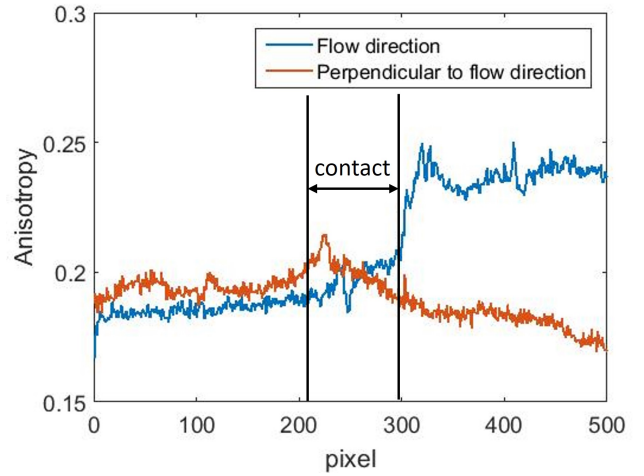
(a) $I_V H$: Intensity with vertical polariser and horizontal analyser



(b) $I_V V$: Intensity with vertical polariser and vertical analyser



(c) Anisotropy r



(d) Anisotropy r along red and blue lines shown in (c).

Figure 6.3: Intensity for VH and VV configurations of the polarisers, and corresponding anisotropy distribution. PAO 8 + Nile Red, pure rolling, $U_e = 150 \text{ mm/s}$, $P_{max} = 287 \text{ MPa}$. Flow direction is bottom to top. Note that in order to visualise the contact clearly, the intensity scales are different in figures (a) and (b). In (c), black circle represents the ball-on-disc contact.

An example is given in figure 6.3, for PAO 8 + Nile Red in pure rolling. Intensity distributions for the VH and VV configurations are respectively in figures 6.3a and 6.3b. The contact is where the image is darker as it is the region of lower film thickness, hence lowest intensity. It is represented by blue dashed circles in figures 6.3a and 6.3b. When the contact is rolling, cavitation develops at the outlet. The corresponding anisotropy map is reported in figure 6.3c. In the contact, identified by a black circle, no variations in the values of the anisotropy are observed. For better visualisation, the anisotropy in the flow direction and perpendicular to the flow direction is reported in figure 6.3d. No substantial change of anisotropy is observed in the contact. As the pressure, hence the viscosity, is maximum at the centre of the contact, the anisotropy should also have a maximum value at the centre of the contact. It is not the case here. The experimental conditions were the same as in Dench *et al.* [141] and they found a maximum viscosity around 5 Pa·s at the centre of the contact, which corresponds to an anisotropy value r around 0.25. It should also be noted that the value of the anisotropy in the contact is around 0.19, while the calibration gave an anisotropy of 0.17 for PAO 8. The difference cannot be attributed to an increase of viscosity in the contact as values outside the contact, where no pressure is applied, are also above 0.17.

These results show that the viscosity cannot be quantified using this technique with a LED based on anisotropy measurements.

6.2.4 Recommendations for future work

The anisotropy technique presented in this section has the potential to provide new knowledge on EHD contacts and viscosity distributions. The technique developed is safe and affordable. The calibration provided the anisotropy-viscosity relationship for PAO fluids, and proved that polymer solutions of PAO + PB fall on the same calibration curve. The technique has the potential to be used in the study of viscosity modifiers and polymer solutions.

In its present state, the technique cannot provide anisotropy maps of an EHD contact, the sensitivity is too low. Recommendations for future improvements are the use of an objective of higher magnification. This might enable a finer measurement of the intensity in the contact. Other materials for the ball and the disc, such as sapphire, or a non-reflective ball made of a black material for example, might also help reduce the noise coming from reflection of the light on the contact surface.

Other techniques can provide viscosity maps of EHD contacts. The advantage of the anisotropy technique is that Nile Red could be used, as it dissolves in PAO oils. In the next section, the fluorescence lifetime spectroscopy technique is presented. A new fluorophore is used in attempt to make this technique suitable for PAO fluids.

6.3 Fluorescence lifetime spectroscopy for viscosity mapping of EHD contacts

Dench *et al.* [140] successfully accessed the local viscosity *in situ* in an EHD contact using fluorescence lifetime spectroscopy. Their study was limited to a hydrophilic system due to the nature of the dye, thioflavin-T. In this section, I explore the possibility of using another molecular rotor, Bodipy C10, to enable the use of this technique with PAO fluids.

6.3.1 Bodipy as a novel fluorophore for viscosity mapping in EHD contacts

With the development of new fluorophores, photo-luminescence techniques have the potential to allow the study of EHD rheology with more appropriate systems and under more extreme conditions than what has been done until now. Bodipy dyes are molecular rotors whose lifetime depends on the viscosity of their surroundings and are temperature-independent. Figure 6.4 shows the increase of the fluorescence lifetime of Bodipy C10 with viscosity. The curves at different temperatures overlap, the dye is not temperature-dependent. The lifetime starts to plateau at a relatively high viscosity, above 10^3 cP. In short, Bodipy dyes can be used as viscosity sensors for viscosities as high as 10^3 mPa·s, and they have the advantage of having long lifetimes [177].

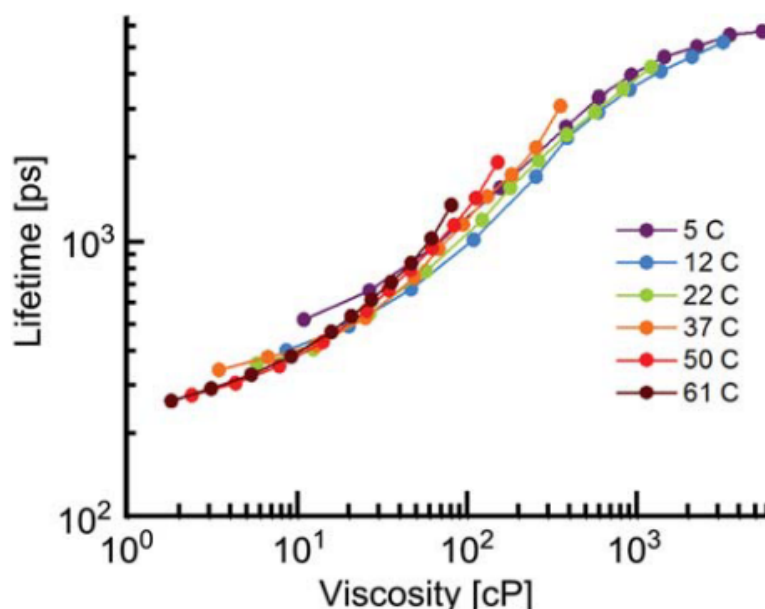


Figure 6.4: Fluorescence lifetime of Bodipy C10 as a function of viscosity measured at different temperatures. The solutions used are mixtures of methanol-glycerol of different viscosities. Adapted from [178].

The molecular structure of Bodipy C10 is given in figure 6.5. Due to their long hydrocarbon tail attached to the phenyl group, Bodipy dyes are soluble in oils. Consequently, they would be ideal fluorophores to investigate the *in situ* viscosity of high-pressure EHD contacts. One disadvantage of Bodipy dyes is their cost. They are expensive compared to their hydrophilic counterparts such as thioflavin-T, which are cheaply available.

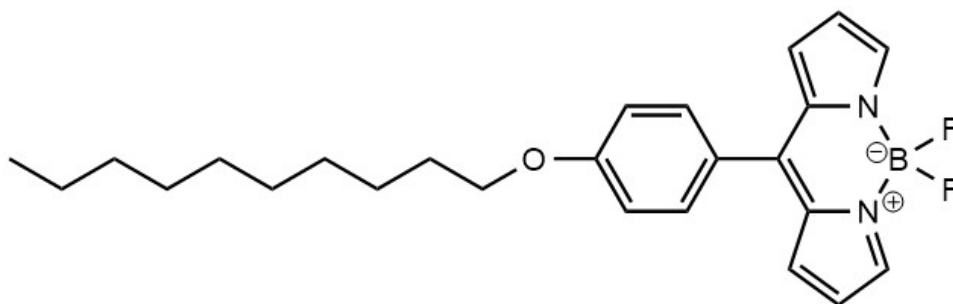


Figure 6.5: Bodipy C10

6.3.2 Materials and methods

The optical setup for the fluorescence lifetime spectroscopy technique is shown in figure 6.6. The ball-on-disc contact is placed on an inverted microscope. The position of the contact is controlled using a motorised microscope stage. The doped lubricant is excited by 400 nm laser pulses. The laser pulses are initially generated at 800 nm by a Tsunami mode-locked Ti:sapphire laser (pulse width 80 fs, frequency 80 MHz), and frequency doubled by a barium borate crystal. The objective is a 20x Olympus UPlanFL, NA 0.5. The emitted photons are detected by a single-photon avalanche photodiode (APD). A Beckel Hickl SPC-152 TCSPC (time-correlated single photon counting) card is connected to both the synchronisation output of the laser and the APD to generate the fluorescence decay curves. All experiments are performed at room temperature, controlled at 22 °C.

For illustration, an example of three consecutive decay curves is given in figure 6.7. The fluid is PAO 8 doped with Bodipy C10, in a cuvette under the objective, at room temperature. For each decay curve, the normalised intensity reaches a value of 1 after the excitation of the dye molecules by a laser pulse. Then the intensity decreases exponentially over time. The lifetime is extracted from a mono-exponential fit of the decay (equation 3.2), which is a good model for Bodipy C10 in PAO 8. The lifetime of Bodipy C10 can be calculated from this mono-exponential fit.

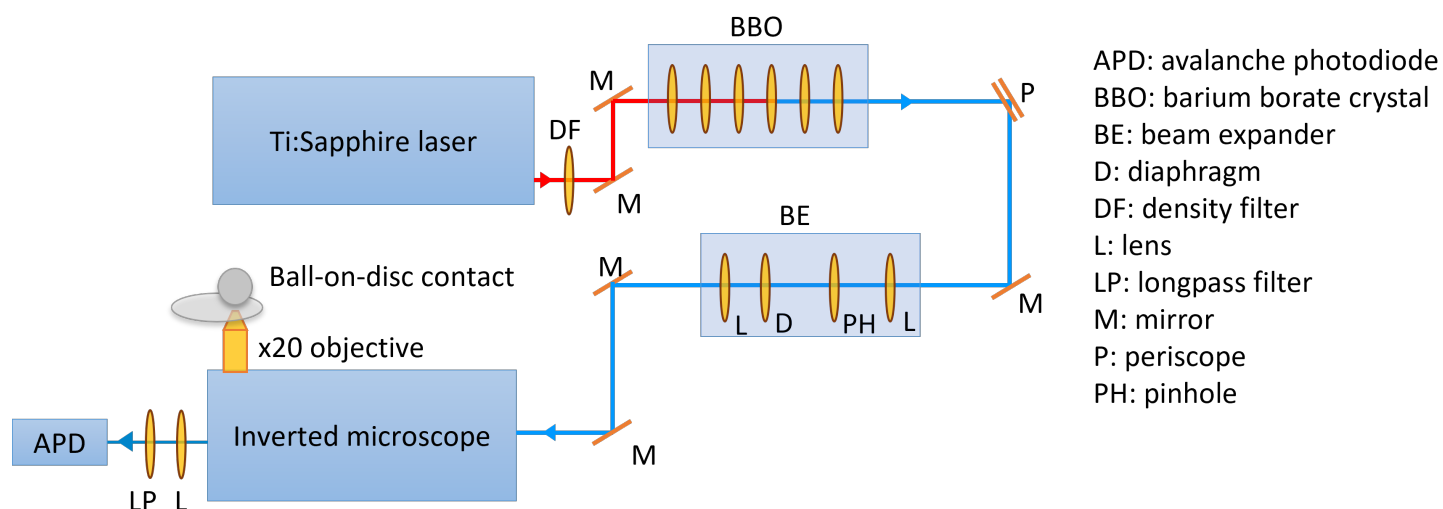


Figure 6.6: Fluorescence lifetime spectroscopy setup

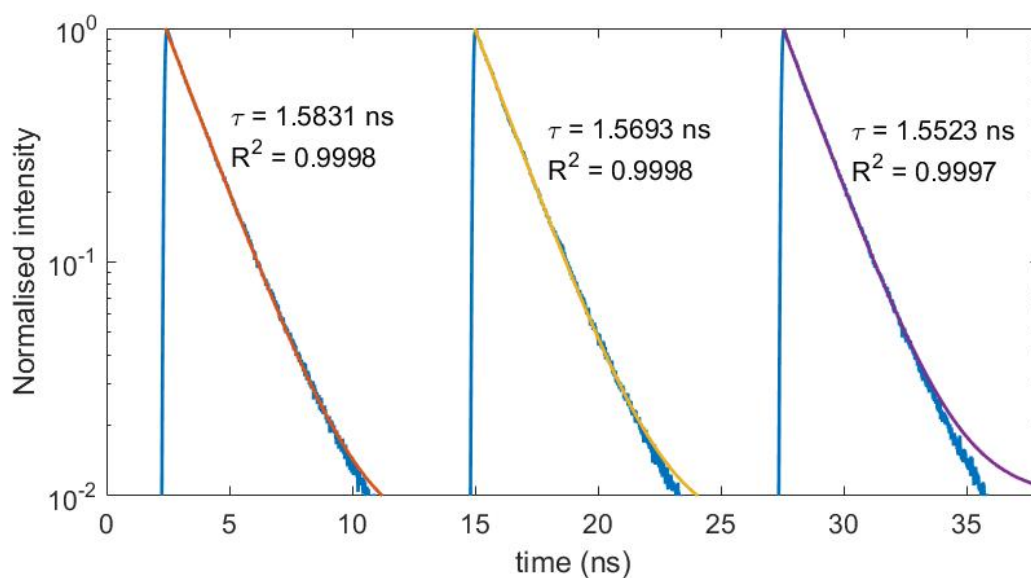


Figure 6.7: Normalised photocount over time for PAO 8 + Bodipy C10 under static conditions. The lifetime τ is given for each of the three decay curves, from a mono-exponential fit. Blue line is the photocount, red, yellow and purple lines are fits.

The test fluids are PAOs of different viscosities doped with Bodipy C10. Bodipy C10 was synthesised by Marina Kuimova at Imperial College London (Department of Chemistry). One test fluid is a polymer solution, Durasyn 145 + 16 wt% PB, chosen to have a viscosity similar to PAO 8. The list of fluids with their viscosity measured with a Stabinger viscometer (Anton-Paar) can be found in table 6.2.

Table 6.2: Fluids used for fluorescence lifetime spectroscopy and viscosity

Fluid	Viscosity at 22 °C (Pa·s)
Isopropanol	0.0022
Ethanol	0.0012
Durasyn 164	0.0342
Durasyn 145	0.0514
SpectraSyn 4 (PAO 4)	0.0287
SpectraSyn 8 (PAO 8)	0.0902
SpectraSyn 10 (PAO 10)	0.1394
SpectraSyn 40 (PAO 40)	1.0671
SpectraSyn 150 (PAO 150)	4.8790
Durasyn 145 + 16 wt% PB	0.1009

6.3.3 Lifetime-viscosity calibration in bulk

The calibration was done in bulk and under static conditions. PMMA cuvettes were filled with the fluids and placed on top of the inverted microscope. The photocounts over time were acquired and the lifetimes calculated using a mono-exponential decay. The resulting calibration curve is shown in figure 6.8. All the fluids align well, including the polymer solution. Bodipy C10 still respond at the highest viscosity, in PAO 150. It confirms that this molecular rotor is a suitable viscosity sensing probe for hydrophobic fluids.

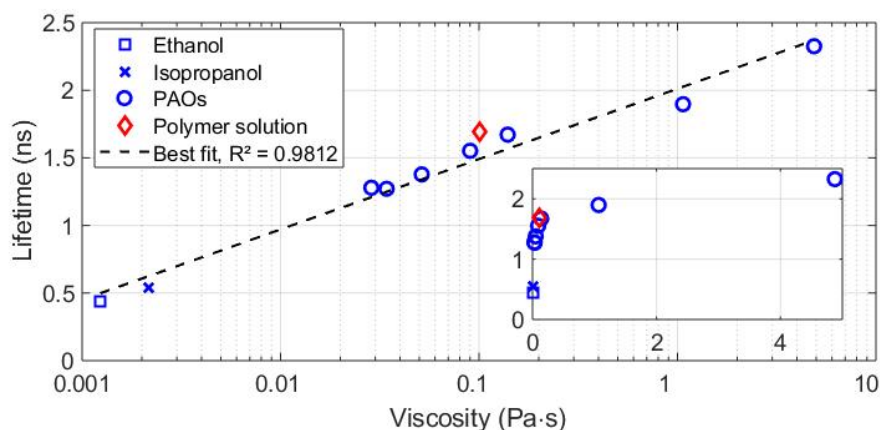


Figure 6.8: Calibration lifetime-viscosity, dotted line is best fit. Dye is Bodipy C10. Polymer solution is highlighted in red. Insert is linear plot.

6.3.4 In situ viscosity maps using fluorescence lifetime spectroscopy

A lifetime map was acquired for PAO 8. As the distribution of pressure is hertzian in the contact, it is expected that the viscosity, hence the lifetime, is heterogeneous in the contact. The ball-on-disc contact consisted of a steel ball and a glass disc. The maximum pressure in the contact was 303 MPa and the entrainment speed was 150 mm/s. The contact was in pure rolling. Photocount decays were measured at 121 positions evenly distributed, following a grid of 11x11 lines. The viscosity was then calculated using the calibration fit. The maps of lifetime and viscosity are reported in figure 6.9. A clear increase in viscosity is seen at the centre of the contact. However, it can be noticed that outside the contact, the viscosity is not homogeneous and varies between 0.12 and 0.25 Pa.s. The viscosity value for PAO 8 should be 0.09 Pa.s outside the contact, where the fluid is not under pressure. Unfortunately, due to the Covid-19 pandemic, this experiment could not be explored further and no other fluid was tested.

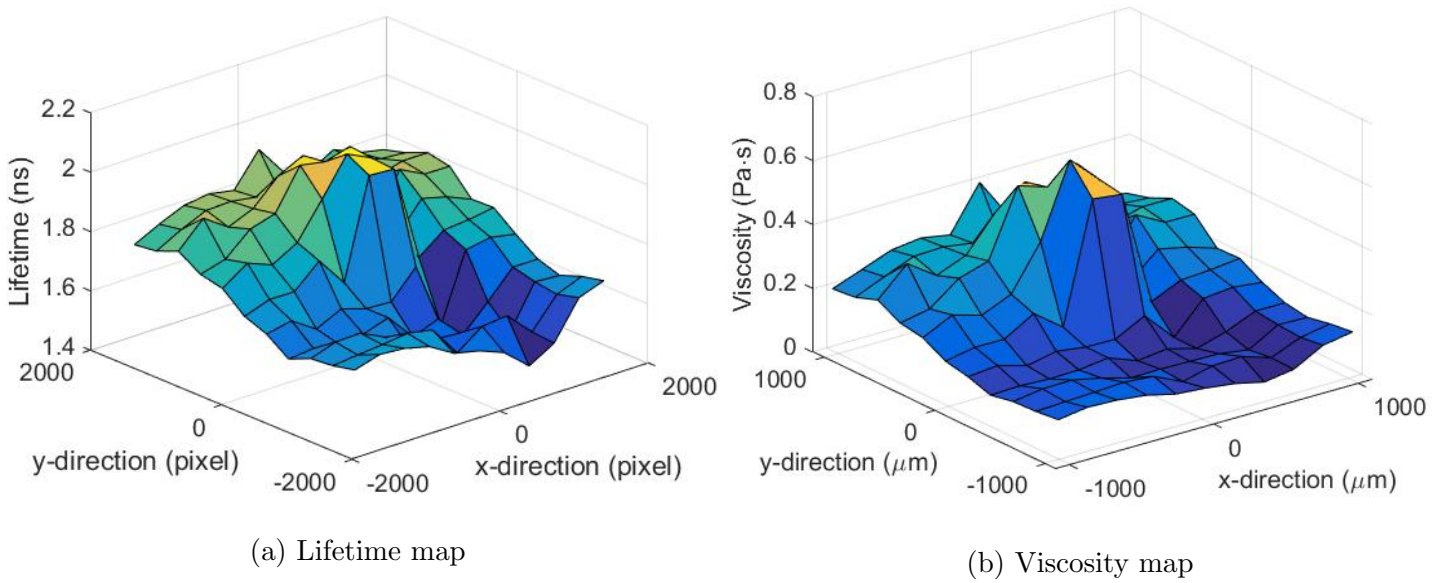


Figure 6.9: Variation of (a) lifetime and corresponding (b) viscosity for PAO 8 doped with Bodipy C10. $P_{max} = 303 \text{ MPa}$, $U_e = 150 \text{ mm/s}$, pure rolling. Theoretical contact radius is $a = 77 \mu\text{m}$.

6.4 Conclusions

In this work, two techniques are developed which show potential of probing the local viscosity in an EHD contact.

Using a LED in the fluorescence anisotropy technique was promising but failed to give satisfactory results. No variation in anisotropy could be detected in the contact. However, the calibration done in bulk was successful. This is encouraging and further improvements of the ball-on-disc optical setups might unlock *in situ* measurements using a LED.

A first viscosity map was obtained for PAO 8 using fluorescence lifetime spectroscopy. Despite an unintended interruption of the experiments, the initial results suggest that the viscosity of hydrophobic systems can be investigated using the molecular rotor Bodipy C10. This is groundbreaking as only aqueous systems had been studied in the past using fluorescence lifetime spectroscopy. The calibration curve also gives encouraging results for the polymer solution, which lifetime aligns well with the other fluids. This observation has to be taken with care as in this case, the polymer molecules (polybutene) are relatively small. With a bigger viscosity modifier, or in the presence of micelles of polymer molecules, the mono-exponential model might have to be changed to a double-exponential decay of the intensity,

$$I(t) = I_1 e^{\frac{-t}{\tau_1}} + I_2 e^{\frac{-t}{\tau_2}}, \quad (6.2)$$

where I_1 , τ_1 and I_2 , τ_2 are the parameters for the slow component (viscosity modifier) and the fast component (base oil), respectively.

Future work should also include the impact of shear stress and pressure on viscosity. This is crucial for viscosity modifiers as the shear-thinning behaviour of polymer solutions is still poorly understood. Knowing the viscosity at the inlet and in the contact would provide incredibly valuable insights.

Chapter 7

Bridging the gap between friction and viscometry at high pressure: estimation of the viscosity-pressure behaviour of a fluid from friction measurements

The high-pressure viscometry of fluids is investigated in this chapter. Two models are proposed to predict the viscosity from friction measurements. Experimental friction and film thickness measurements are performed for two fluids, then the data is fed into the fitting procedure using the two models. Results are compared with the high-pressure viscometry data.

7.1 Introduction

Knowing the rheology of lubricants at high pressure is essential to lubricant design, and is key for increasing fuel economy. The viscosity of a lubricant changes significantly with pressure. For example, inflection points in the logarithm of viscosity against pressure curves were reported as early as 1949 [30]. The pressure-viscosity relationship of lubricants mainly drives friction in non-conforming contacts under elastohydrodynamic (EHD) conditions [179].

Although numerous studies have focused on the viscosity response at high pressure, many questions are still debated, such as on the role of thermal effects and on the limiting shear stress [52, 15], as well as the possible glass transition experienced by the fluid [180]. Bridging the gap between rheology and viscosity under severe conditions of pressure and

shear have generated considerable recent research interest [15, 141, 36, 181]. Given the rheology, friction under EHD conditions can be fairly well estimated using numerical solvers [181, 182, 183, 184] or molecular dynamic simulations [185, 24]. However, only few studies have investigated the reverse approach, that is estimating the viscosity from friction. High-pressure rheometry is with no doubt the most straightforward and effective method to measure the viscosity at high pressure. Nevertheless, high-pressure rheometers are not widely available, while the tools and equipment to measure friction are common. The development of an alternative method based on friction would be greatly beneficial when a high-pressure rheometer is not available.

Dench *et al.* [141] successfully developed an in-situ fluorescence anisotropy technique to access the local viscosity of a polyalphaolefin in a ball-on-disc EHD lubricated contact. They also estimated the viscosity at pressures up to 720 MPa using friction measurements and compared their results with measurements from high-pressure rheometers. Despite showing promising results, accessing the local viscosity requires a very advanced optical setup, thus cannot be easily implemented. Another drawback is that their viscosity calculation from friction requires an estimation of the viscosity-pressure coefficient, meaning that a good knowledge of the fluid behaviour is required prior to the analysis.

Estimating the viscosity from friction is challenging. The friction is a single value measured of a contact where the normal pressure, hence the viscosity of a lubricant in a contact, is not necessarily homogeneous. Thermal effects in the contact, due to friction heating, is more obvious at high pressures and may affect lubricant viscosity. Performing friction tests at high pressures is technically difficult, yet recently Zhang and Spikes [15] measured friction in an EHD point contact at very high pressure (mean pressure up to 5 GPa).

This chapter aims at providing an accessible method to derive the rheology of a fluid from friction measurements. The viscosity of two fluids were estimated solely from film thickness and friction measurements obtained in a ball-on-disc apparatus under elastohydrodynamic conditions. The appropriateness and the limitation of this approach are assessed.

7.2 Methodology

To assess how well friction measurements can be used to determine the viscosity of lubricant at different pressures, friction and film thickness measurements were carried out. To minimise the effect of frictional heating, temperature correction was done to access the isothermal shear stress. The viscosity-pressure relationship was then estimated using a non-linear least square error procedure. The methodology is illustrated by the flow chart in figure 7.1. Two fluids were selected for this work, the dibasic acid ester

Bis(2-ethylhexyl) sebacate (DEHS), and a group 4 oil, Spectrasyn™ 8 (PAO 8). DEHS was purchased from Sigma-Aldrich and PAO 8 was provided by ExxonMobil. Both were used as provided.

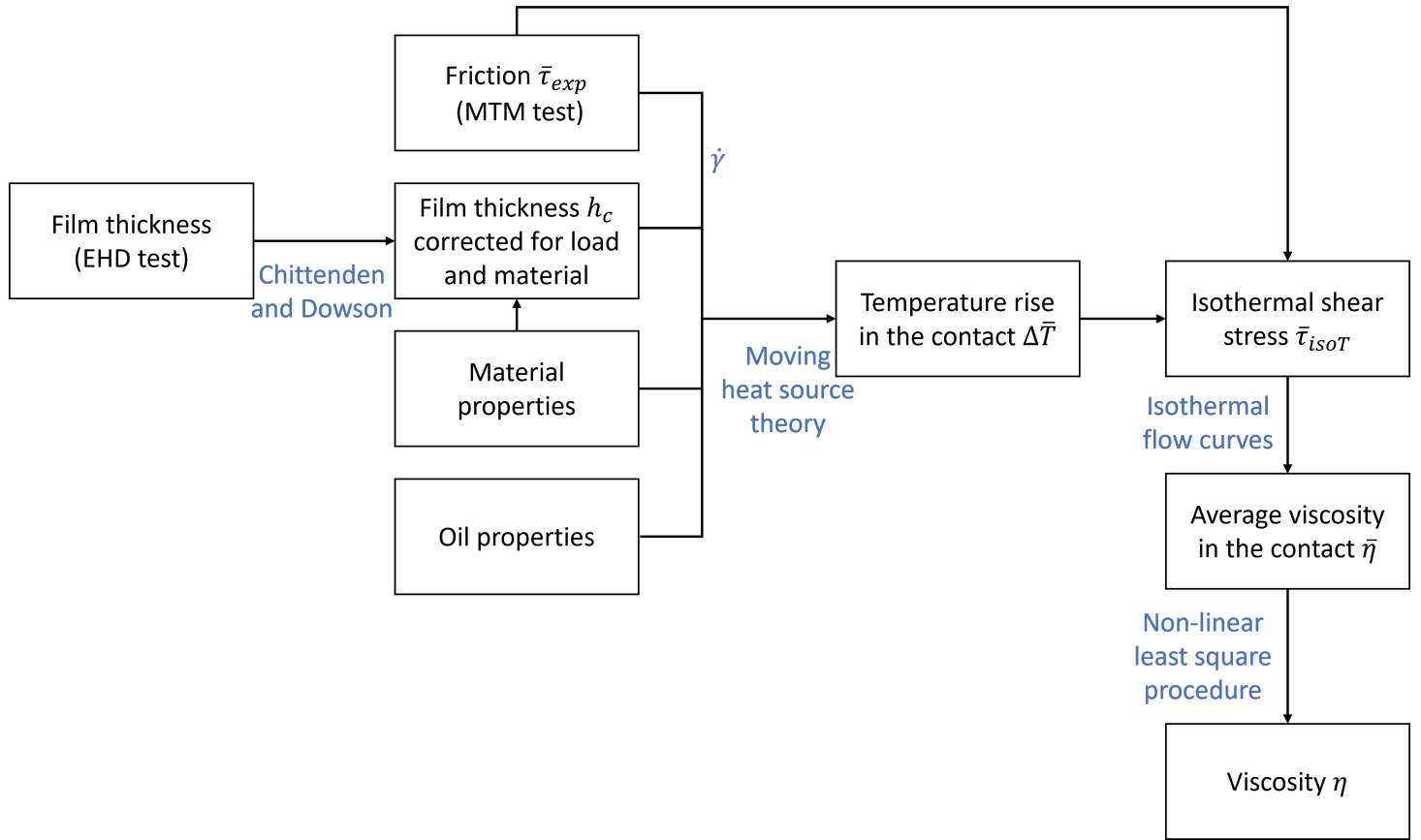


Figure 7.1: Flow chart for viscosity prediction from friction and film thickness tests

7.2.1 Low shear viscosity

The dynamic viscosity η obtained with an Anton Paar SVM 3000 Stabinger viscometer are listed in table 7.1. Viscosity indices (VI) were then calculated based on these values.

Table 7.1: Viscosity of tested fluids

Fluid	Dynamic viscosity η (mPa·s)			VI
	30 °C	40 °C	100 °C	
PAO 8	60.5	38.6	6.2	140
DEHS	14.5	10.4	2.8	158

7.2.2 EHD friction

Friction under elastohydrodynamic conditions was measured using a Mini Traction Machine, MTM (PCS Instruments, Acton, UK). A 19 mm diameter ball was loaded against a disc, both immersed in a lubricant bath, and the frictional force between the two surfaces was measured by a force transducer. The normal load applied on the ball ranged from 10 N to 75 N with the standard loading system and can be as low as 2 N to 10 N with a low load loading system. Tests were performed at room temperature (25 °C), 30 °C, 40 °C, and 50 °C. Various materials were chosen for the ball and the disc to provide a wide range of pressures and assess the role of the thermal effect. They are listed in table 7.2 along with their mechanical and thermal properties.

Table 7.2: Properties of the materials used in the friction tests

	Ball E (GPa)	Disc E (GPa)	Disc and ball ν (-)	Ball K (W/mK)	Disc K (W/mK)	Ball c (J/kgK)	Disc c (J/kgK)	Ball ρ (kg/m ³)	Disc ρ (kg/m ³)
Glass	75	75	0.22	1.05	1.05	840	840	2500	2500
AISI 52100 steel	207	207	0.29	21	21	475	475	7810	7810
WC	737	630	0.2	61	65	120	170	14300	14800
ZrO ₂	210	-	0.32	2.4	-	278	-	5680	-
Sapphire	-	345	0.3	-	23.1	-	753	-	3985

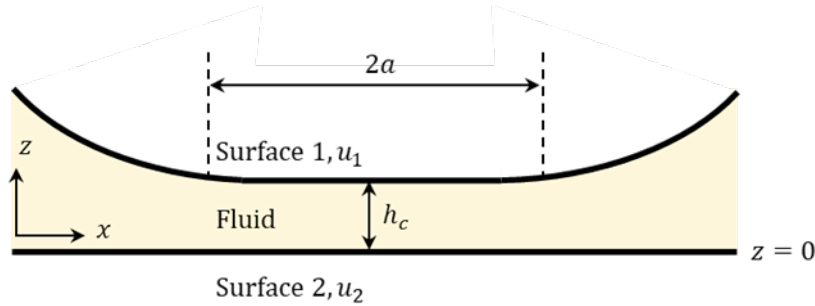


Figure 7.2: Schematic of a ball-on-disc contact of radius a and central film thickness h_c . In the elastohydrodynamic regime, the two surfaces are fully separated by the lubricant film (not to scale).

An EHD point contact is shown schematically in figure 7.2. The pressure distribution $P(r)$ in the ball-on-disc point contact is assumed Hertzian,

$$P(r) = P_{max} \sqrt{1 - \left(\frac{r}{a}\right)^2} \quad (7.1)$$

where P_{max} is the maximum pressure in the contact, r is the radial position and a is the

radius of the contact defined by

$$a = \left(\frac{3}{4} \frac{WR}{E^*} \right)^{1/3} \quad (7.2)$$

where W is the normal load, R is the equivalent radius, equal here to the radius of the ball, and E^* is the reduced modulus. The maximum pressure, located at the centre of the contact, is

$$P_{max} = \frac{3}{2} \frac{W}{\pi a^2}, \quad (7.3)$$

and the mean pressure is defined by

$$\bar{P} = \frac{2}{3} P_{max}. \quad (7.4)$$

The mean pressure ranges for the pairs of specimens used for the friction tests are listed in table 7.3.

Table 7.3: Reduced moduli and pressure ranges for the tested pairs of specimens

Ball/Disc	E^* (GPa)	Mean pressure range (MPa)
Glass/Glass	39	125 – 410
Glass/Steel	58	163 – 533
Steel/Glass	58	279 – 533
Steel/Steel	113	253 – 828
ZrO ₂ /Glass	58	278 – 531
ZrO ₂ /Steel	112	430 – 823
ZrO ₂ /WC	166	559 – 1016
Glass/WC	70	315 – 573
WC/Glass	71	318 – 579
Steel/WC	168	564 – 1024
WC/Steel	175	578 – 1051
WC/WC	354	925 – 1681

The temperatures of interest (nominal temperatures) in this work are 30 °C for DEHS and 40 °C for the PAO. These temperatures were selected to match the temperatures of the available viscometry data used for comparison. For each load, the entrainment speed was 0.3 m/s and the slide-roll ratio (SRR) ranged between 0 and 20 %.

From the frictional force F and the mean pressure yields the average shear stress in the contact

$$\bar{\tau}_{exp} = \mu \bar{P} \quad (7.5)$$

where $\mu = F/W$ is the coefficient of friction. The strain rate is defined by

$$\dot{\gamma} = \frac{SRR U_e}{100 h_c} = \frac{\Delta U}{h_c} \quad (7.6)$$

where h_c is the central film thickness, U_e the entrainment speed and ΔU the sliding speed.

7.2.3 EHD film thickness

The central thickness of the lubricant film was measured by optical interferometry using an EHD2 rig (PCS Instruments, Acton, UK). A steel ball, immersed in a temperature controlled lubricant bath was loaded at 20 N against a coated glass disc. The ball was driven by the disc, resulting in a pure-rolling condition. The tests were performed at seven temperatures ranging from 25 °C to 100 °C. The entrainment speed ranged from 0.1 m/s to 3 m/s. Results from film thickness measurements were fitted using equation 7.7 where T is the temperature of the contact and $a_0, \dots, a_8$ are the fitting parameters. This fit is a polynomial surface of 3rd order with respect to entrainment speed and 2nd order with respect to temperature.

$$h_c(T, U_e) = a_0 + a_1 U_e + a_2 U_e^2 + a_3 U_e^3 + a_4 T + a_5 T^2 + a_6 U_e T + a_7 U_e^2 T + a_8 U_e T^2, \quad (7.7)$$

Film thickness values at a normal load of 20 N at various temperature and entrainment speed can then be estimated via interpolations. For this fit, only the 5 closest temperatures to the nominal temperatures, respectively 30 °C and 40 °C for DEHS and the PAO, were used. This ensured a coefficient of determination R^2 above 0.98 for both fluids. The values obtained requires adjustment since the friction tests were carried out at different loads and with different materials than the film thickness measurement. The film thickness values corresponding to the conditions of the friction tests were estimated using the equation proposed by Chittenden and Dowson [172]

$$h_c \propto W^{-0.073} E^{*-0.117}. \quad (7.8)$$

The film thickness measured for the PAO at three temperatures is plotted in figure 7.3, with their fit using equation (7.7) and estimation using (7.8). The influence of slide-roll ratio is assumed negligible as it was kept under 20 % [186]. Hence, the film thickness values measured in pure rolling are used without further correction for the rolling-sliding contacts.

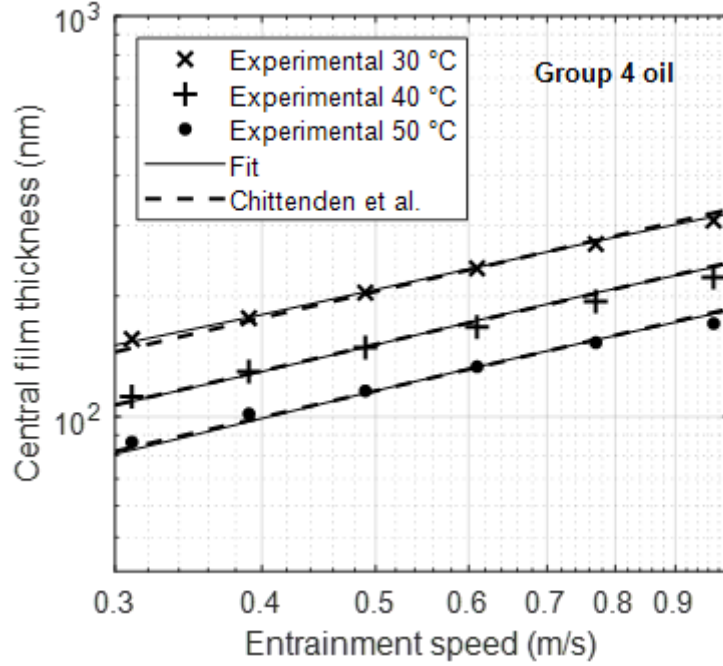


Figure 7.3: Central film thickness for PAO 8, measured, fitted using equation (7.7) and estimated using [172].

7.3 Thermal effects in the contact and correction

Heat is generated in the lubricant film during rubbing by shear heating and compressive heating, especially at high pressure, high shear stress and with specimens having low thermal conductivities. The increase of the oil and surface temperatures in a contact reduces lubricant viscosity and leads to a reduction in friction [123]. Knowing the temperature rise in the contact is thus necessary for the understanding of the frictional response of the oil. It is also needed to estimate the isothermal shear stress, that is to estimate the friction without any temperature effect.

Note that the thickness of the lubricant film in a contact is driven by the conditions at the inlet of the contact. Based on the test conditions chosen for the friction tests, the inlet shear heating was assumed negligible. Thus, the film thickness from equations (7.7) and (7.8) was obtained at the supply temperature and entrainment speed of the friction test, i.e., no temperature correction was performed.

7.3.1 Temperature rise in the contact

The dissipation of heat in the contact in steady state is given by

$$K_{oil} \frac{\partial^2 T}{\partial z^2} = -q_v \quad (7.9)$$

where K_{oil} is the thermal conductivity of the oil and z the direction perpendicular to the plane of the contact. The rate of heat generation by friction per unit volume q_v is defined by

$$q_v = \frac{\bar{\tau}_{exp} \Delta U}{h_c}. \quad (7.10)$$

Equation (7.9) represents the convection across the contact. The film thickness of the oil h_c is much smaller than the radius of the contact a , hence the gradients of temperature in the plane of the contact (x-y plane in figure 7.2) are negligible with respect to the conduction across the contact [187]. It is assumed that the rate of heat generation through the thickness is constant, and a Couette shear applies to the oil. Following the calculations employed by Archard [188], the integration of the equation of the dissipation of heat through the thickness gives

$$\bar{T}_{oil} = T_0 + \Delta \bar{T}_{surf} + \Delta \bar{T}_{oil} \quad (7.11)$$

where $\bar{T}_{oil}$ is the mean temperature of the oil in the contact, T_0 is the supply temperature, $\Delta \bar{T}_{surf}$ is the mean temperature rise of the contact surfaces and $\Delta \bar{T}_{oil}$, given by

$$\Delta \bar{T}_{oil} = \frac{q_v h_c^2}{8 K_{oil}}, \quad (7.12)$$

is the mean temperature rise of the oil in the contact.

The thermal conductivity of the oil K_{oil} is assumed constant with temperature but varies with pressure. The thermal conductivity values for DEHS and the PAO were obtained, for pressures up to 1.1 GPa, by extraction of the data for the most similar fluids found in Larsson and Andersson [189]. At higher pressures, the values were estimated by interpolation (2nd order polynomial fit). The thermal conductivities at various pressures are listed in table 7.4.

Table 7.4: Estimated thermal conductivity K_{oil} (W/mK)

Pressure (GPa)	DEHS	PAO 8
0.1	0.19	0.18
0.5	0.25	0.24
1	0.31	0.32
1.5	0.35	0.38

In the case of two contact surfaces of different materials, the calculation of the mean temperature rise of the contact surfaces is not straightforward as the heat is partitioned, with αq going to one surface (surface 1) and $(1 - \alpha)q$ going to the other surface (surface 2), with α the heat partition fraction. The heat partition coefficient is calculated by equating the mean temperatures of the two surfaces [190]. This is made possible by the assumption that the film is thin enough, so that its temperature gradient is negligible and does not decouple the temperatures of the two surfaces [191]. Using this, the interfacial temperature rise in a sliding Hertzian contact was provided by Francis [53] and expressed in terms of the temperature rises of the two contact surfaces $\Delta\bar{T}_1$ and $\Delta\bar{T}_2$ if each of them were to receive all of the frictional heat by

$$\frac{1}{\Delta\bar{T}_{surf}} = \frac{1}{\Delta\bar{T}_1} + \frac{1}{\Delta\bar{T}_2}. \quad (7.13)$$

In the friction tests performed in this study, because the slide-roll ratio is kept low (under 20 %), both surfaces are moving relatively fast with respect to the contact. Thus, the temperature rises $\Delta\bar{T}_1$ and $\Delta\bar{T}_2$ are calculated using the moving heat source theory, taken from Archard [188] and adapted to the ball-on-flat contact case by Zhang *et al* [123], and are given by

$$\Delta\bar{T}_i = \frac{1}{(2\pi K_i \rho_i c_i)^{0.5}} \left(\frac{2a}{U_e} \right)^{0.5} q_v h_c, \quad i = 1, 2, \quad (7.14)$$

where K_1 and K_2 are the thermal conductivities of the surface materials, ρ_1 and ρ_2 their densities, and c_1 and c_2 their specific heat capacity.

7.3.2 Isothermal shear stress

With the estimation of the temperature rise in the contact, the measured friction can be linked to the estimated contact temperature. Consequently, the isothermal shear stress, i.e., the shear stress at the supply temperature, can be accessed by performing an appropriate interpolation [123]. For each fluid and each load, the sets of data ($\bar{\tau}_{exp}$, $\dot{\gamma}$, $\bar{T}_{oil}$) from the three friction tests having the test temperature the closest to the nominal temperature (30 °C for DEHS and 40 °C for PAO) were considered. These sets of data were restricted to the values at SRRs above 1 %. At lower SRRs, the temperature rise is negligible hence the shear stress does not need to be temperature corrected. The data sets were also restricted to temperature rises below 10 °C. Higher temperature rise estimations are not reliable enough to be included. Then, these restricted sets of data were fitted simultaneously to the following polynomial equation

$$\bar{\tau}_{fit}(T) = c_0 + c_1\zeta + c_2\zeta^2 + c_3\zeta^3 + c_4T + c_5T^2 + c_6\zeta T \quad (7.15)$$

where $\bar{\tau}_{fit}$ is the average shear stress by fitting, $T = \bar{T}_{oil}$ is the mean temperature of the oil in the contact, $\zeta = \ln \dot{\gamma}$ and $c_0, \dots, c_6$ are the fitting parameters. The latter are obtained using a least square error method.

The isothermal average shear stress in the contact at a given load, at the supply temperature T_0 , is given by

$$\bar{\tau}_{isoT}(T_0) = \bar{\tau}_{exp}(\bar{T}_{oil}) + (\bar{\tau}_{fit}(T_0) - \bar{\tau}_{fit}(\bar{T}_{oil})). \quad (7.16)$$

Henceforth, $\bar{\tau} = \bar{\tau}_{isoT}(T_0)$ denotes the isothermal average shear stress at the supply temperature, from the friction tests. The average shear stress (symbols) and isothermal average shear stress (solid lines) for the ester, at different mean contact pressures, are plotted in figure 7.4.

The number of data points included for the estimation of isothermal average shear stress depends on the applied pressure and the choice of the rubbing surfaces (i.e. various length of solid lines in figure 7.4) since only data points with less than 10 °C contact temperature rise are used. As the applied load increases or a decrease in surface thermal conductivity results in an increase in contact temperature, the number of data included is reduced.

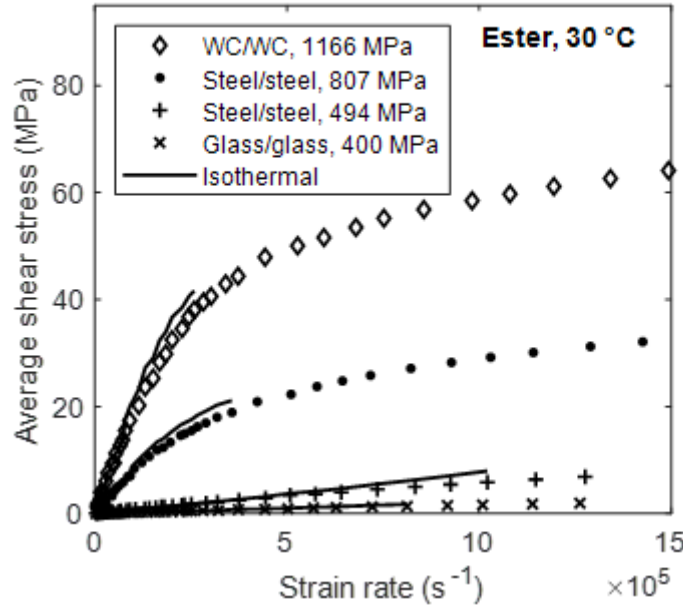


Figure 7.4: Average shear stress against strain rate for DEHS at four mean contact pressures, accessed using different pairs of contact materials. The supply temperature is 30 °C. The solid lines represent the estimated isothermal average shear stress, capped at a maximum temperature rise in the contact of 10 °C.

7.3.3 Average viscosity

Figure 7.5 shows five isothermal flow curves ($\bar{\tau} - \dot{\gamma}$) of the ester at different mean contact pressures, along with the linear regressions used for the calculation of the average viscosity $\bar{\eta}$. The average viscosity $\bar{\eta}$

$$\bar{\eta} = \frac{\bar{\tau}}{\dot{\gamma}}. \quad (7.17)$$

is calculated only using data points in the Newtonian region of the flow curves, where the isothermal average shear stress is a linear function of the strain rate.

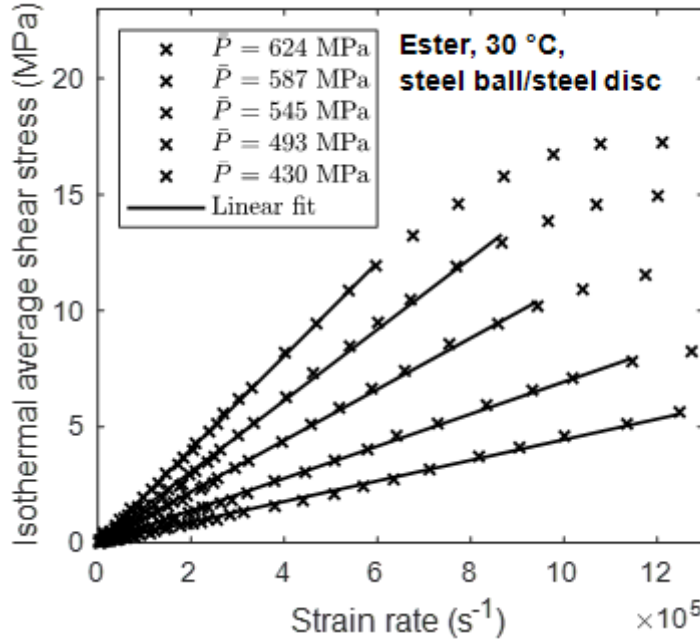


Figure 7.5: Isothermal average shear stress against strain rate for DEHS at five mean contact pressures. The solid lines are the corresponding linear regression of the linear regions, which slopes are the average viscosities $\bar{\eta}$.

7.4 Linking friction measurements to lubricant rheology

The friction force F generated in the contact is

$$F = \int_0^{2\pi} \int_0^a \tau(r, \theta) r dr d\theta, \quad (7.18)$$

where r, θ are the polar coordinates in the contact and $\tau(r, \theta)$ is the local shear stress at the point (r, θ) . Expressing the friction force equation (7.18) in terms of strain rates and viscosities yields

$$F = \int_0^{2\pi} \int_0^a \dot{\gamma}(r, \theta) \eta(r, \theta) r dr d\theta \quad (7.19)$$

where $\dot{\gamma}(r, \theta)$ and $\eta(r, \theta)$ are the local strain rate and local viscosity, respectively, at the point (r, θ) . In this study, the following assumptions are made within the contact:

- The temperature is constant, as an isothermal calculation was performed for the shear stress.
- The viscosity is hence only a function of the pressure.
- The film thickness is constant as it is mainly driven by the inlet viscosity.
- The flow is Couette, hence the strain rate is constant (as the film thickness is constant).
- The contact is axisymmetric, there is no dependence in θ .

Based on these assumptions, equation (7.19) can be simplified to

$$F = 2\pi a^2 \dot{\gamma} \int_0^1 \eta(P(\rho)) \rho d\rho \quad (7.20)$$

with $\rho = r/a$ the dimensionless radial position. From this expression, the link between friction and viscosity becomes apparent. It shows that with a functional form carefully chosen for the viscosity, supported by a reliable numerical procedure, it is possible to access the rheology of a fluid from its friction data. Rearranging equation (7.20) to obtain

$$\bar{\eta} = \frac{F}{\pi a^2 \dot{\gamma}} = 2 \int_0^1 \eta(\rho) \rho d\rho, \quad (7.21)$$

the average viscosity $\bar{\eta}$ derived from the EHD friction is expressed as a function of the local viscosity η , which is only dependent on the local pressure.

7.5 Non-linear least square procedure

Given N data points $(P_i, \bar{\eta}_i)$ from friction experiments, the viscosity $\eta(P, \boldsymbol{\alpha})$, where $\boldsymbol{\alpha}$ is the vector of parameters to be fitted, is determined by the least square method. The parameters giving the best fit of the experimental data are found by minimising the error $\mathcal{E}$, defined by

$$\mathcal{E}(\boldsymbol{\alpha}) = \sum_{i=1, N} r_i^2(\boldsymbol{\alpha}) \quad (7.22)$$

where r_i is the residual between the experimental data $(P_i, \bar{\eta}_i)$ and the fitted value $\eta(P_i, \boldsymbol{\alpha})$.

The problem being non-linear, Newton's method is used to find $\boldsymbol{\alpha}$. With an initial set of values $\boldsymbol{\alpha}^{(0)}$, the subsequent iterations are given by

$$\boldsymbol{\alpha}^{(n+1)} = \boldsymbol{\alpha}^{(n)} - \mathbf{H}^{-1} \mathbf{g} \quad (7.23)$$

where $\boldsymbol{\alpha}^{(n)}$ is the n^{th} iteration of $\boldsymbol{\alpha}$, $\mathbf{g}$ is the gradient vector of $\mathcal{E}$, defined by

$$g_j = 2 \sum_{i=1, N} r_i \frac{\partial r_i}{\partial \alpha_j} \quad (7.24)$$

and $\mathbf{H}$ is the Hessian matrix of $\mathcal{E}$, defined by

$$H_{jk} = 2 \sum_{i=1, N} \left(\frac{\partial r_i}{\partial \alpha_j} \frac{\partial r_i}{\partial \alpha_k} + r_i \frac{\partial^2 r_i}{\partial \alpha_j \partial \alpha_k} \right). \quad (7.25)$$

7.6 Functional forms for the viscosity

In this work, two different functional forms to describe effect of pressure on viscosity were selected and compared, a Barus-like form and an Eyring-like form.

The first form, as used by Dench *et al.* [141], is similar to the Barus equation 2.3, with the pressure-viscosity coefficient described by a 3rd order polynomial in the maximum contact pressure P_{max}

$$\eta = \eta_0 e^{\alpha_1 P_{max} + \alpha_2 P_{max}^2 + \alpha_3 P_{max}^3}. \quad (7.26)$$

Using this expression for the viscosity and the Hertz equation (7.1) for the pressure, equation (7.21) is now written as

$$\bar{\eta} = \frac{F}{\pi a^2 \dot{\gamma}} = 2\eta_0 \int_0^1 e^{\alpha_1 P_{max} \xi + \alpha_2 P_{max}^2 \xi^2 + \alpha_3 P_{max}^3 \xi^3} \xi d\xi \quad (7.27)$$

with $\xi = \sqrt{1 - \rho^2}$ and

$$\boldsymbol{\alpha} = \begin{pmatrix} \eta_0 \\ \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} \quad (7.28)$$

is determined by minimising the error with the least square method as stated in equations 7.23 - 7.25.

Writing equation (7.27) in the logarithmic form

$$\ln(\bar{\eta}) = \ln(\eta_0) + \ln(Q(P_{max}, \alpha_1, \alpha_2, \alpha_3)) \quad (7.29)$$

where

$$Q(P_{max}, \alpha_1, \alpha_2, \alpha_3) = 2 \int_0^1 e^{\alpha_1 P_{max} \xi + \alpha_2 P_{max}^2 \xi^2 + \alpha_3 P_{max}^3 \xi^3} \xi d\xi \quad (7.30)$$

is the integral term. The N residuals between the experimental data $(P_{max_i}, \bar{\eta}_i)$ and the

fitted values $\eta(P_{max_i}, \eta_0, \alpha_1, \alpha_2, \alpha_3)$ are

$$r_i = \ln(\eta_0) + \ln(Q(P_{max_i}, \alpha_1, \alpha_2, \alpha_3)) - \ln(\bar{\eta}_i), \quad i = 1, \dots, N. \quad (7.31)$$

It should be noted that minimising the error in equation (7.31) is not equivalent to minimising the error in

$$t_i = \eta(P_{max_i}, \eta_0, \alpha_1, \alpha_2, \alpha_3) - \bar{\eta}_i. \quad (7.32)$$

The logarithmic form is biased towards smaller values, reducing the accuracy of the fit for smaller values and, in this case, smaller pressures.

The second functional form is based on the shear thinning Eyring model

$$\tau = \tau_e \operatorname{asinh}\left(\frac{\eta \dot{\gamma}}{\tau_e}\right). \quad (7.33)$$

Setting the pressure-viscosity relationship as exponential and the Eyring stress τ_e as a linear function of pressure, and substituting them into equation (7.18), the shear stress is given by

$$\frac{F}{\pi R^2} = \tau(P, \dot{\gamma}, \alpha_0, \dots, \alpha_5) = 2 \int_0^1 (\alpha_4 + P\xi\alpha_5) \operatorname{asinh}\left(\frac{\dot{\gamma} e^{\alpha_0 + P\xi\alpha_1 + P^2\xi^2\alpha_2 + P^3\xi^3\alpha_3}}{\alpha_4 + P\xi\alpha_5}\right) \xi d\xi \quad (7.34)$$

This time, there are six $\alpha_0, \dots, \alpha_5$ parameters to be fitted with the least square error procedure to match the experimental data points $(\bar{P}_i, \dot{\gamma}_i, \bar{\tau}_i)$ from the friction tests. The expression of the residuals is

$$r_i = \tau(P_i, \dot{\gamma}_i, \alpha_0, \dots, \alpha_5) - \bar{\tau}_i. \quad (7.35)$$

7.7 Sensitivity analysis

To evaluate the robustness of the method, the sensitivity against each input variable was evaluated. This was achieved by a standard method of propagation of small perturbations in the model. Let

$$\mathbf{R}(\boldsymbol{\alpha}, x_1, \dots, x_n) = \frac{\partial \mathcal{E}}{\partial \boldsymbol{\alpha}} \quad (7.36)$$

with $\boldsymbol{\alpha}$ the parameters that minimize the error in the least square procedure and $x_1, \dots, x_n$ the variables, it follows

$$\mathbf{R}(\boldsymbol{\alpha}, x_1, \dots, x_n) = 0 \quad (7.37)$$

and, by differentiation,

$$\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} d\boldsymbol{\alpha} + \frac{\partial \mathbf{R}}{\partial x_1} dx_1 + \dots + \frac{\partial \mathbf{R}}{\partial x_n} dx_n = \mathbf{0}. \quad (7.38)$$

The logarithmic differentiation is preferred here, in order to express the uncertainties as relative values, giving

$$\frac{\partial \mathbf{R}}{\partial \ln \boldsymbol{\alpha}} \frac{d\boldsymbol{\alpha}}{\boldsymbol{\alpha}} + \frac{\partial \mathbf{R}}{\partial \ln x_1} \frac{dx_1}{x_1} + \dots + \frac{\partial \mathbf{R}}{\partial \ln x_n} \frac{dx_n}{x_n} = \mathbf{0}. \quad (7.39)$$

The change $d\boldsymbol{\alpha}$ induced in $\boldsymbol{\alpha}$ by the perturbations $dx_1, \dots, dx_n$ is bounded by

$$\left\| \frac{d\boldsymbol{\alpha}}{\boldsymbol{\alpha}} \right\| \leq \left\| \left(\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} \right)^{-1} \frac{\partial \mathbf{R}}{\partial \ln x_1} \right\| \left\| \frac{dx_1}{x_1} \right\| + \dots + \left\| \left(\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} \right)^{-1} \frac{\partial \mathbf{R}}{\partial \ln x_n} \right\| \left\| \frac{dx_n}{x_n} \right\| \quad (7.40)$$

where $\| \cdot \|$ is the Frobenius norm.

In the Barus-like case, the variables x are P and $\bar{\eta}$, and they are P , $\dot{\gamma}$ and $\bar{\tau}$ in the Eyring-like case. For the variables from friction tests, uncertainties were estimated either from calibration of the MTM machine or from actual measurements. The uncertainty for the central film thickness was estimated by comparing the measured values with the prediction calculated using the point contact equation (7.8) from Chittenden and Dowson [172], effectively by comparing the solid lines to the dashed lines in figure 7.3. Finally, uncertainties for strain rate, pressure and viscosity were calculated using the equation of propagation

$$dx(\mathbf{y}) = \frac{\partial x}{\partial y_i} dy_i \quad (7.41)$$

where x is a function of n variables y . Table 7.5 lists the uncertainties for the experimental variables.

Table 7.5: Uncertainties and their determination method.

Parameter	Uncertainty	Method
Ball load W	0.5 %	Change in successive load calibration of rig
Speed U	0.9 %	Change in successive speed calibration of rig
Friction force F	0.6 %	Change in successive transducer calibration of rig
Equivalent radius R	1.5 %	Measure with caliper
Area of contact $A = \pi a^2$	4.0 %	Measure by imaging of the contact
Film thickness h_c	3 to 5 %	Comparison with prediction

For example, for the Barus-like functional form case, after using the equation of propagation (7.41) for the viscosity (equation (7.17)) and the pressure (equation (7.3)),

equation (7.40) gives

$$\begin{aligned} \frac{\partial \mathbf{R}}{\partial \ln \boldsymbol{\alpha}} \frac{d\boldsymbol{\alpha}}{\boldsymbol{\alpha}} + \frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \ln F} \frac{dF}{F} + \frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \dot{\gamma}} \frac{\partial \dot{\gamma}}{\partial \ln(\Delta U)} \frac{d\Delta U}{\Delta U} + \frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \dot{\gamma}} \frac{\partial \dot{\gamma}}{\partial \ln h_c} \frac{dh_c}{h_c} \\ + \frac{\partial R}{\partial P} \frac{\partial P}{\partial \ln W} \frac{dW}{W} + \left(\frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \ln A} + \frac{\partial R}{\partial P} \frac{\partial P}{\partial \ln A} \right) \frac{dA}{A} = 0. \end{aligned} \quad (7.42)$$

Defining transfer matrices as

$$\mathbf{g}^F = \left(\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} \right)^{-1} \frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \ln F} \quad (7.43a)$$

$$\mathbf{g}^{\Delta U} = \left(\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} \right)^{-1} \frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \dot{\gamma}} \frac{\partial \dot{\gamma}}{\partial \ln(\Delta U)} \quad (7.43b)$$

$$\mathbf{g}^{h_c} = \left(\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} \right)^{-1} \frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \dot{\gamma}} \frac{\partial \dot{\gamma}}{\partial \ln h_c} \quad (7.43c)$$

$$\mathbf{g}^W = \frac{\partial R}{\partial P} \frac{\partial P}{\partial \ln W} \quad (7.43d)$$

$$\mathbf{g}^A = \left(\frac{\partial \mathbf{R}}{\partial \boldsymbol{\alpha}} \right)^{-1} \left(\frac{\partial \mathbf{R}}{\partial \bar{\eta}} \frac{\partial \bar{\eta}}{\partial \ln A} + \frac{\partial R}{\partial P} \frac{\partial P}{\partial \ln A} \right) \quad (7.43e)$$

we can assess the influence of each experimental parameter on viscosity. The norms of the transfer matrices give the contribution of each experimental uncertainty on the error of the fitting parameters. Their values are reported in table 7.6. For the Barus-like form, the area of contact is the main source of error. The current experimental uncertainty is 4.0 %, (see table 7.5), consequently by multiplying by the value of the norm of the corresponding transfer matrix, it propagates in the fit and leads to an error on the fit parameters of 15 %. On the same note, if the error on the fit parameters from the area of contact had been imposed to be less than 10 %, it would have been required to keep the experimental uncertainty for the area of contact under 2.7 %. Due to the complexity of the Eyring form and of the procedure to propagate the error, the calculation of the errors in that case was unsuccessful and no values are reported here.

Table 7.6: Contribution of experimental uncertainties on the sensitivity of the fit.

Transfer matrix	Barus-like form
$\ \mathbf{g}^F\ $	1.00
$\ \mathbf{g}^{\Delta U}\ $	1.00
$\ \mathbf{g}^{h_c}\ $	1.00
$\ \mathbf{g}^W\ $	3.65
$\ \mathbf{g}^A\ $	3.76

7.8 Results

Based on the analysis discussed above, the lines of best fit for the rheology of DEHS and PAO 8 is stated in table 7.7

Table 7.7: Best fit for the viscosity derived from friction for DEHS and PAO 8

P (GPa)	Viscosity ($Pa \cdot s$)			
	DEHS		PAO 8	
	Barus-like form	Eyring-like form	Barus-like form	Eyring-like form
0	0.01	0.03	0.04	0.05
0.1	0.05	0.09	0.17	0.20
0.2	0.18	0.22	0.61	0.66
0.3	0.52	0.55	1.91	1.97
0.4	1.39	1.34	5.23	5.18
0.5	3.39	3.14	12.57	12.13
0.6	7.56	7.06	26.92	25.58
0.7	15.54	15.06	51.78	48.85
0.8	29.57	30.31	90.46	85.23
0.9	52.37	57.21	144.95	136.90
1	86.81	100.53	215.22	204.04
1.1	135.35	163.37	299.16	284.45
1.2	199.55	243.88	393.24	373.85
1.3	279.71	332.15	493.85	466.90
1.4	374.68	409.96	598.59	558.52
1.5	482.20	455.44	707.42	645.03

The viscosity-pressure curves are reported in figure 7.6 for the two functional forms, along with the high-pressure viscometry for comparison. It should be noted that this gives the rheological relationship between viscosity and pressure. The viscosity here is the low-shear viscosity with no thermal effects and is not to be confused with the average viscosity derived from friction measurements. Likewise, the pressure is the pressure experienced by the fluid and not the average pressure in the ball-on-disc contact.

Although there are some reservations expressed in the literature about the potential use of friction measurements as a way of accessing high-pressure rheometry of fluids [192], the estimated viscosity here shows good agreement with the reference viscometry data, up to 1 GPa. At low pressure, under 300 MPa, the estimation using the Barus-like functional form gives more satisfactory results compared to the Eyring-like functional form. This is not surprising as the use of a logarithm in the calculation of the residual equation (7.31) tends to decrease the accuracy towards the lowest values of viscosity. At medium pressure, the two functional forms overlap and for PAO 8 between 0.3 and 0.8 GPa, the estimated viscosity is extremely close to the high-pressure viscometry data. At high pressure, above 1 GPa, the estimated viscosity in both forms and for the two fluids displays a change in

slope with a slower increase in viscosity. For PAO 8, the deviation between estimated and measured viscosity increases at these pressures. The models failed to introduce an inflexion point in this region which would have given a more appropriate trend at high pressure.

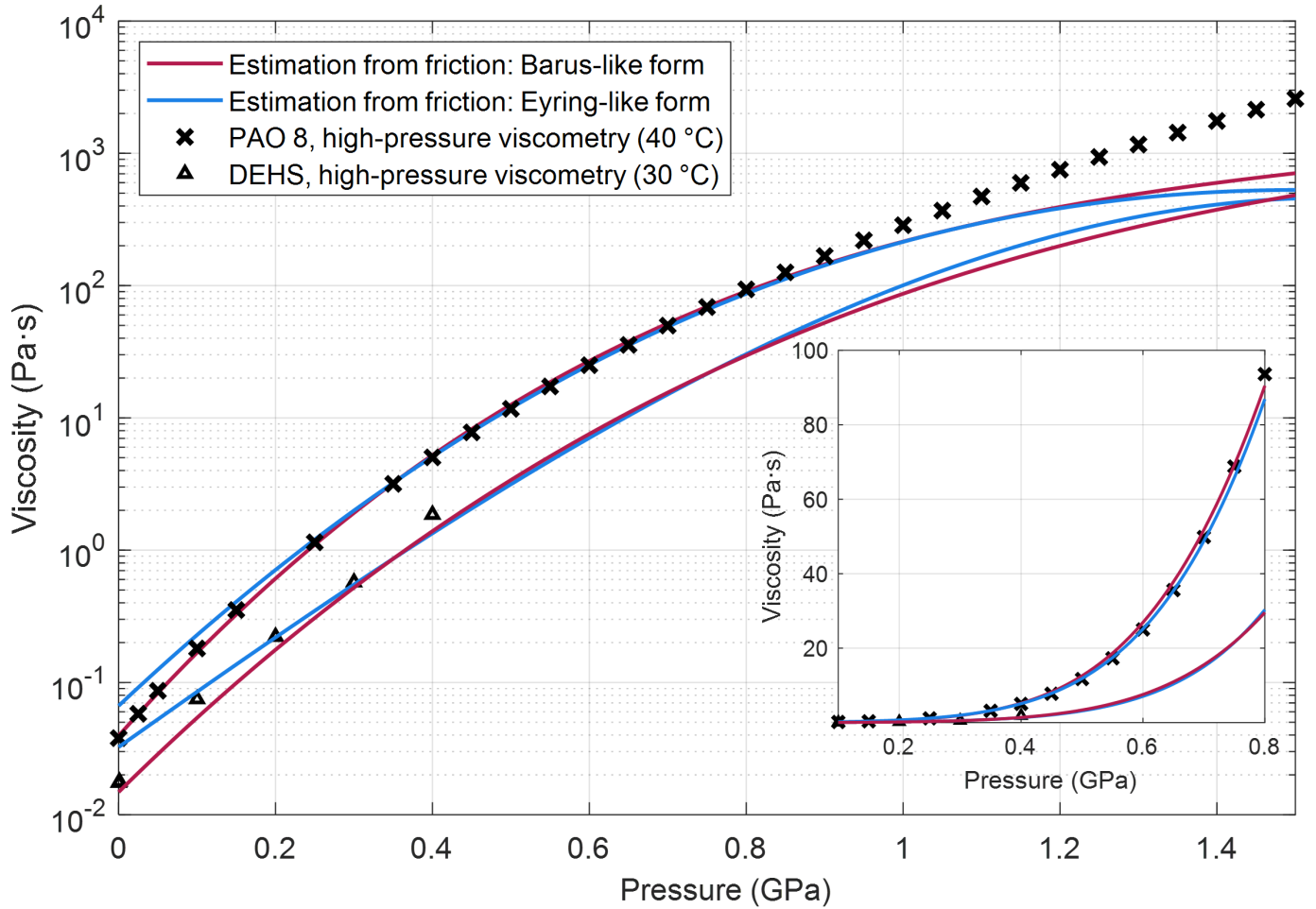


Figure 7.6: Viscosity-pressure behaviour for DEHS and PAO 8. The solid lines are the viscosity estimated from friction using the two functional forms, the black symbols are the high-pressure rheometry data provided by Bair (private communication). Insert highlights the region 0-0.8 GPa in linear-linear axes.

In figure 7.7, the shear stress calculated with the Eyring-like form is compared with the isothermal shear stress from the friction experiments. Despite a light scattering, there is a clear trend around the line of equality, the estimated shear stress matches the experimental value. A larger deviation can be noticed for PAO 8 in the highest shear stresses: the estimated values are higher than the experimental ones, the values go above the line of equality around $\ln(\tau_{MTM}) = -4$. This is congruent with the higher deviation observed in the viscosity at the highest pressures.

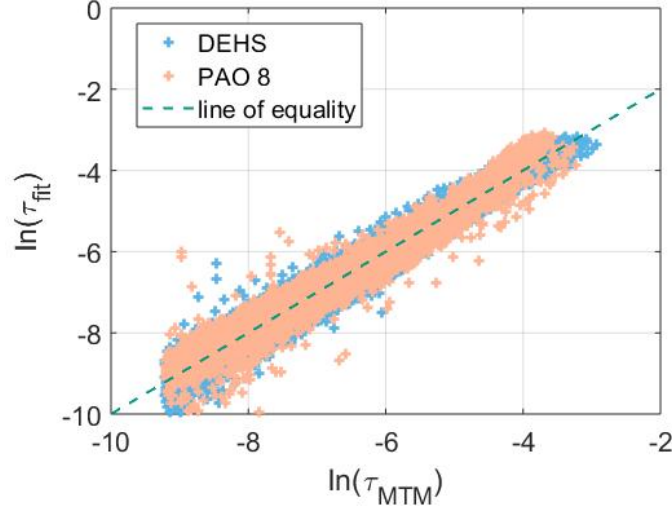


Figure 7.7: Comparison between measured and estimated shear stress. τ_{MTM} is the isothermally corrected shear stress from friction experiments, τ_{fit} is the shear stress calculated using the viscosity estimated with the Eyring-like form.

Two other models, equations 7.44, were tried in order to integrate the thermal consideration directly in the form and not through an isothermal correction of the shear stress. The aim was also to predict the viscosity at other temperatures by introducing the temperature dependence in the form and using in the fitting procedure all the friction data collected at other temperatures. Unfortunately, the outputs were far from satisfactory, these models were more complex, with a too high sensitivity towards the initial values of the parameters and giving an unrealistic dependence of viscosity with temperature.

$$\eta(P, T) = e^{\alpha_0 + \alpha_1 P + \alpha_2 P^2 + \alpha_3 P^3 + \frac{\alpha_4}{T + \alpha_5}} \quad (7.44a)$$

$$\eta(P, T) = e^{\alpha_0 + \alpha_1 P + \frac{\alpha_2}{P + \alpha_3} + \frac{\alpha_4}{T + \alpha_5}} \quad (7.44b)$$

7.9 Conclusions

A method to predict the viscosity-pressure behaviour of fluids has been developed in this work. Two functional forms, a Barus-like form and a Eyring-like form, have been successfully utilised to estimate the viscosity up to 1.5 GPa for DEHS and PAO 8, from friction measurements.

This study strengthens the existing link between rheology and tribological performance. From friction measurements, this method enables the prediction of viscosity through a careful processing and fitting of the experimental data.

The method requires the measurement of friction across a wide range of pressures. Using specimens made of materials having different mechanical properties, the mean pressure in the contact ranged between 125 MPa and 1.7 GPa. The isothermal shear stress was calculated to remove the thermal effects generated during rubbing. These values obtained from friction tests were linked to the viscosity by integration of the viscosity over the contact. The viscosity was estimated using a least square procedure.

Comparing predicted values with experimental values from high-pressure viscometry, both forms give satisfactory results in the medium pressure range (0.3 to 0.8 GPa). At lower pressures, the Barus-like form performed better. At higher pressures, the predicted values deviate more from the experimental values and the estimation fails to follow the viscosity-pressure trend above 1 GPa.

Possible improvements include the use of a functional form that would make possible the presence of an inflection point at high pressure. Experiments have shown that the viscosity at high pressure is complex cannot be interpolated from low pressure values, as an inflection point is sometimes observed in the viscosity-pressure curves at high pressure [30]. Another refinement would be the integration of the temperature dependence in the model. This would simplify the processing of the data as no isothermal correction would be needed anymore. It would also make the method very powerful as the prediction of the viscosity could be done at any desired temperature (within the range of temperatures of the friction tests) and not just at one temperature at a time. A last modification could be to constraint the estimated viscosity at ambient pressure. This value of the viscosity is known, as can be measured with high precision with the Stabinger viscometer. Imposing this value would improve the prediction at low pressure. However, this lowers the number of degrees of freedom and might impact the results at high pressures. This change was tried with the Barus-like and Eyring-like forms but the deviations at high pressures were larger. A different functional form is needed to implement this improvement.

Chapter 8

Conclusions and future work

The aim of this thesis was to understand the behaviour of lubricants in the elastohydrodynamic lubrication regime, in particular in the case of viscosity modifier-containing solutions. The complex non-Newtonian responses were explored across scales, including at the micro-scale flow profiles, *in situ* chemical analysis, *in situ* viscosity mapping and at the macro-scale the prediction of the viscosity at high pressures.

Does the flow of polymer solutions deviate from a Couette flow, and what are the possible mechanisms involved? This work showed that the velocity profiles of polymer and copolymer solutions can indeed deviate from a Couette flow. Slip and plugs were observed. Polymer depletion and adsorption, shear response and film thickness, as well as polymer size were considered in the discussion.

What drives the film thickness of polymer solutions, and do polymer molecules enter the contact? The results suggest that no depletion or aggregation of polymer occurred at the inlet and in the contact for the tested fluid. This supports that inlet shear-thinning and shear-heating are the mechanisms inducing film thickness reduction. This is a key finding that can direct the design of viscosity modifiers to increase their efficiency.

Can friction be used to predict the high-pressure viscometry of lubricants? The viscosity-pressure relationship of two fluids was successfully predicted, proving that the viscometry can be derived from standard friction and film thickness tests. This is very valuable for tribologists who do not have access to a high-pressure viscometer. It also takes forward the discussion on the possibility, or not, to bridge the gap between friction and high-pressure viscometry.

This chapter summarises the main findings and conclusions, presents the limitations and suggests recommendations for further work.

8.1 Summary of findings

1. The through-film velocity profiles of polymer solutions in an EHD contact were investigated using a phosphorescence imaging velocimetry technique. Velocity profiles were reconstructed, based on the *in situ* phosphorescence response of the fluid. A new methodology including an improved background correction was developed to access velocity profiles in cases where the film thickness was as low as 150 nm. The technique was validated with neat oils displaying Couette flows.

Polymer and copolymer solutions were selected and fully characterised. The size of the polymers in solution was measured by light scattering. QCM was used to investigate the adsorption behaviour of the polymers and copolymers. Adsorption occurred in all cases. The shear-thinning response was quantified at medium and high shear rates, showing substantial shear-thinning of the polymer solutions. The film thickness of the fluids was measured by optical interferometry and it was found that the thickness of polymer solutions reduces at high SRR due to shear-thinning.

Velocity profiles of solutions of polystyrene in ester showed that interfacial slip occurs, but not in all cases. Slip is favoured when the polymer has a high molecular weight, the polymer concentration is high and the solvent molecules have a high mobility at the contact surfaces. Results with copolymer solutions suggested that adsorption of the copolymer on the contact surfaces impacts the velocity profiles, plugs near the surfaces were observed. This supports the assertion that adsorbed polymers form a viscous layer.

2. A novel technique using Raman spectroscopy was designed to perform chemical analyses *in situ* in the tribological EHD contact and track potential changes at the inlet, in the contact and at the outlet. This technique enables the detection of changes in lubricant composition. The aim was to assess if changes observed in the film thickness of polymer solutions are produced by a change in polymer concentration at the inlet of the contact.

This technique was applied to solutions of polybutene in PAO. The characterisation of the rheological response of these polymer solutions showed that they shear thin. Their film thickness was also measured and compared against their low-shear dynamic viscosity. This analysis suggested that these polymer solutions are likely to experience inlet shear-thinning, impacting their film thickness.

Results showed no change in the Raman spectra between measurements at the inlet and in the contact, indicating that for these polymer solutions, the polymer concentration does not increase or decrease at the inlet. Hence, the change in film thickness observed for polymer solutions is not induced by aggregation or depletion

of polymer molecules at the inlet. From the results, it was also confirmed that the polymer molecules enter and flow through the contact.

3. Preliminary studies of local viscosity measurements *in situ* in an EHD contact using fluorescence were carried out. Despite a promising lifetime-viscosity calibration, the viscosity in the contact could not be mapped using fluorescence anisotropy with a LED. The spatial resolution with this technique was too low to detect the variations of viscosity in the EHD contact.

With the fluorescence lifetime spectroscopy technique, promising results were achieved. An oil-soluble molecular rotor, Bodipy, was used in PAO. This dye proved to be a suitable viscosity sensor, even at high viscosities, as the calibration was performed up to 5 Pa·s. A first viscosity map of PAO 8 in the tribological contact was obtained, showing that this technique can be applied to actual lubricants.

4. It was demonstrated that the viscosity-pressure behaviour of a fluid can be predicted from friction measurements. Two models for the viscosity were proposed, based on a Barus-like form and an Eyring-like form. A precise methodology was developed to take into account thermal effects in the frictional response. A least square procedure was applied to minimise the error.

This methodology was applied to two fluids, DEHS and PAO 8. Their viscosity-pressure response was successfully predicted up to 1.5 GPa and compared to high-pressure viscometry values. It was found that the Barus-like model gives a better prediction of the viscosity at low pressures (under 0.3 GPa). The results at medium to high pressures (up to 0.8 GPa) were very satisfactory for the two fluids for both models. Only PAO 8 could be compared with the experimental data in this range of pressure, and it was found that the prediction was in very good agreement with the benchmark data, the two sets of values overlapped. Above 0.8 GPa, larger deviations were obtained, the models failed to accurately predict the viscosity-pressure behaviour. The models were not able to generate the expected inflection point in the viscosity-pressure curve. This means that this method needs improvements, with more friction data at high pressure for example, or a different functional form for the viscosity.

This work highlights the strong interconnection between rheology and friction. The main takeaway is that the high-pressure viscometry of a fluid can be fairly well predicted from friction tests, which is invaluable when no high-pressure viscometers are available.

8.2 Limitations

New methods and experimental techniques were implemented in this work. Optical techniques offer the advantage of giving direct access to the tribological contact but entail some limitations.

In all optical techniques, transparent surfaces are needed, but glass and sapphire are not typical materials found in engineering components, hence the use of these materials move the experiments away from real-life applications. Another drawback of the Raman spectroscopy and the phosphorescence velocimetry techniques is that the discs used have to be thin enough for the objective to be in focus in the thin film of lubricant in the contact. This limits the pressure that can be applied in the contact as some of the discs were breaking for maximum contact pressures as low as 200 MPa.

In order to have enough intensity and a sufficient signal-to-noise ratio, the film thickness has to be above ~ 150 nm in the phosphorescence velocimetry technique and above ~ 1 μm for the Raman spectroscopy technique. This limitation depends on the system as other systems might give a higher intensity than the systems used in this work, hence potentially be studied at lower film thicknesses. For the Raman technique, this limitation on film thickness means that the film thickness is much higher than the size of the polymer molecules (~ 50 nm). If a film thickness in the range of the size of the polymer molecules is used, aggregation or depletion of polymer may occur at the inlet. The thinner the film thickness, however, the higher the relative noise from the contact surfaces.

Limitations specific to the phosphorescence velocimetry technique include the need for a background correction, due to the fluorescence and phosphorescence of the contact surfaces. The background correction was done by running the same test with a dye-free solution. Not only this was a challenging step as a slight misalignment of the contact during the acquisition of the background image would make the corrected images impossible to process. But it also limits the number of tests that can be done with the same solution, as the pot cannot be cleaned before pouring the dye-free solution, meaning this solution gets slightly contaminated with dye for every test. It should be noted that the dye is relatively expensive, as well as the PAA-PS copolymers. Another limitation is that the entrainment speed and SRR were restricted by the lifetime of the dye. To reconstruct the flow profile, the excited dye molecules have to travel a distance equal to at least the diameter of the laser excitation spot so that fluid flow at the proximity of the bottom and top contact surfaces can be deconvoluted. A higher shear leads to stronger thermal effects that might impact the velocity profiles.

8.3 Recommendations for future work

It is clear that the optical techniques developed in this work can be improved. The Raman spectroscopy technique has only been applied to viscous fluids due to the limitation on the film thickness. A first modification would be to trigger the disc to always take measurements at the same position. As the rotation of the disc is not perfectly straight, the contact slightly moves in and out of focus during one rotation. With triggering, less noise would be collected from the contact surfaces as the acquisition would always occur in focus in the contact. This would increase the sensitivity of the technique and would allow the measurement of Raman spectra of thinner films.

The use of different polymers chosen specifically for their shear-thinning properties would be interesting. Choosing a system which permanently shear thins at low shear rates would unlock the study of shear-thinning, *in situ* in the contact, if the peaks of the broken molecules are different in the Raman spectra. Comparing the spectra at the inlet and in the contact under different shear conditions would help understand the shear-thinning mechanisms of polymer solutions. This was not achieved with the current setup and polymer systems due to the relatively small size of the polymer molecules.

Finally, other transparent materials can be considered for Raman spectroscopy. Sapphire has strong peaks in the region $400\text{--}800\text{ cm}^{-1}$, making the analysis of peaks from the polymer solution very difficult and requiring deconvolution. Diamond could be complementary as has only one sharp peak around 1330 cm^{-1} [193].

Improvements for the phosphorescence velocimetry technique include the optimisation of spatial resolution. This would enable experiments at lower SRRs as the time needed for the fluid to travel a distance equal to the diameter of the laser spot would be reduced. This could be achieved by using an objective with a larger numerical aperture, which would reduce the size of the laser spot. The advantage of low SRRs is the suppression of thermal effects induced by shear heating.

It is also recommended to change and improve the current procedure for background correction. The current method requires the preparation of two solutions, one with a dye and one dye-free. For the study of copolymer solutions, this requirement caused important costs as the copolymer was expensive. This could be overcome by a numerical analysis of the phosphorescence and fluorescence response of the contact surface, so that the background correction is done numerically rather than experimentally. However, this is challenging as many factors have to be considered, such as the film thickness, the shape of the laser spot, the lifetime of the dye.

Concerning the prediction of the viscosity-pressure behaviour from friction, a key refinement would be the use of a functional form of the viscosity that enables the presence of an inflection point in the viscosity-pressure curve. Unfortunately, the two forms used

in this work could not meet this, leading to a deviation of the viscosity at high pressure compared with the benchmark data.

Another natural progression would be to include a temperature dependence in the functional form of the viscosity, so that the raw friction data can be fed into the model without the need to calculate the isothermal shear stress.

Another possibility to obtain better results at high pressures would be to run friction tests at higher contact pressures. This can now be done thanks to the development of the ETM machine by PCS Instruments. Contact pressures up to 5 GPa can be reached, and the advantage is that the geometry is similar to the one used in the MTM, so results would be comparable. However, the thermal effects would be even larger at higher pressures, thus an amelioration of the temperature rise estimation might be needed in this case.

To further extend the understanding of EHD lubrication, the following questions should be explored:

- What is the shear-thinning behaviour of polymer solutions at the contact inlet? Could a measurement of the viscosity at the inlet be used to estimate inlet shear rate? The fluorescence lifetime spectroscopy technique could be used to probe the local viscosity at the inlet, *in situ*.
- What happens at the inlet and what is the flow profile of polymer solutions when the size of the polymer molecules is in the same order of magnitude, or just a bit smaller, than the film thickness?
- How to estimate accurately the film thickness of fluids which are subjected to inlet shear-thinning, inlet shear-heating or slip?
- How are inlet shear-thinning and slip interlinked? It was shown that polymer solutions shear thin at low shear rates, and slip was observed in their velocity profile. It would be interesting to investigate the effect of inlet shear-thinning, or of any mechanism leading to a drop of viscosity at the inlet, on slip.
- Can the viscosity-pressure relationship of polymer solutions be predicted from friction? To which extent would shear-thinning, adsorption and other mechanisms observed in this work impact the methodology?

These improvements would aid our understanding of the rheological responses of lubricants, across scales.

References

- [1] RAC Foundation. FAQs about road transport and the environment.
- [2] GOV.UK. Energy and environment: data tables (ENV) - Greenhouse gas emissions (ENV02) - ENV0201.
- [3] The European Parliament and the Council of the European Union. Regulation (EC) No 443/2009 of the European Parliament and of the Council of 23 April 2009 setting emission performance standards for new passenger cars as part of the Community's integrated approach to reduce CO₂ emissions from light-duty vehicles. *Official Journal of the European Union*, (L140):1–15, 2009.
- [4] The European Parliament and the Council of the European Union. Regulation (EU) 2019/631 of the European Parliament and of the Council of 17 April 2019 setting CO₂ emission performance standards for new passenger cars and for new light commercial vehicles, and repealing Regulations (EC) No 443/2009 and (EU) No 510/2011. *Official Journal of the European Union*, 62(L111):13–53, 2019.
- [5] K. Holmberg, P. Andersson, and A. Erdemir. Global energy consumption due to friction in passenger cars. *Tribology International*, 47:221–234, 3 2012.
- [6] R. Taylor and B. de Kraker. Shear rates in engines and implications for lubricant design. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 231(9):1106–1116, 9 2017.
- [7] R. M. Mortier, M. F. M. F. Fox, and S. T. Orszulik. *Chemistry and technology of lubricants*. Springer, 2010.
- [8] Technical Committee of Petroleum Additive Manufacturers in Europe (ATC). Lubricant Additives: Use and Benefits. Technical report, 2016.
- [9] T. Stöhr, B. Eisenberg, and M. Müller. A New Generation of High Performance Viscosity Modifiers Based on Comb Polymers. *SAE International Journal of Fuels and Lubricants*, 1(1):2008–01, 10 2008.

- [10] S. Morgan, Z. Ye, R. Subramanian, and S. Zhu. Higher-molecular-weight hyperbranched polyethylenes containing crosslinking structures as lubricant viscosity-index improvers. *Polymer Engineering & Science*, 50(5):911–918, 5 2010.
- [11] USV (Ultra Shear Viscometer) — Products — PCS Instruments.
- [12] S. Bair. A New High-Pressure Viscometer for Oil/Refrigerant Solutions and Preliminary Results. *Tribology Transactions*, 60(3):392–398, 5 2017.
- [13] MTM (Mini Traction Machine) — Products — PCS Instruments.
- [14] ETM (Extreme pressure Traction Machine) - PCS Instruments.
- [15] J. Zhang and H. Spikes. Measurement of EHD Friction at Very High Contact Pressures. *Tribology Letters*, 68(1):1–12, 3 2020.
- [16] Y. Cohen and A. B. Metzner. Apparent Slip Flow of Polymer Solutions. *Journal of Rheology*, 29(1):67–102, 2 1985.
- [17] J. Lu, T. Reddyhoff, and D. Dini. A study of thermal effects in EHL rheology and friction using infrared microscopy. *Tribology International*, 146(May 2019):106179, 2020.
- [18] P. Ehret, D. Dowson, and C. M. Taylor. On lubricant transport conditions in elastohydrodynamic conjunctions. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 454(1971):763–787, 1998.
- [19] A. Ponjavic, L. di Mare, and J. S. S. Wong. Effect of pressure on the flow behavior of polybutene. *Journal of Polymer Science Part B: Polymer Physics*, 52(10):708–715, 5 2014.
- [20] P. Sperka, I. Krupka, and M. Hartl. Lubricant flow in thin-film elastohydrodynamic contact under extreme conditions. *Friction*, 4(4):380–390, 12 2016.
- [21] S. Jeffreys, L. Di Mare, X. Liu, N. Morgan, and J. S. Wong. Elastohydrodynamic lubricant flow with nanoparticle tracking. *RSC Advances*, 9(3):1441–1450, 2019.
- [22] S. Bair and C. McCabe. A study of mechanical shear bands in liquids at high pressure. *Tribology International*, 37(10):783–789, 10 2004.
- [23] B. Galmiche, A. Ponjavic, and J. S. Wong. Flow measurements of a polyphenyl ether oil in an elastohydrodynamic contact. *Journal of Physics Condensed Matter*, 28(13), 2016.

- [24] J. P. Ewen, C. Gattinoni, J. Zhang, D. M. Heyes, H. A. Spikes, and D. Dini. On the effect of confined fluid molecular structure on nonequilibrium phase behaviour and friction. *Physical Chemistry Chemical Physics*, 19(27):17883–17894, 7 2017.
- [25] A. Martini, H. Y. Hsu, N. A. Patankar, and S. Lichter. Slip at high shear rates. *Physical Review Letters*, 100(20):206001, 5 2008.
- [26] D. Savio, N. Fillot, P. Vergne, and M. Zaccheddu. A model for wall slip prediction of confined n-alkanes: Effect of wall-fluid interaction versus fluid resistance. *Tribology Letters*, 46(1):11–22, 4 2012.
- [27] J. P. Ewen, D. M. Heyes, and D. Dini. Advances in nonequilibrium molecular dynamics simulations of lubricants and additives. *Friction*, 6(4):349–386, 12 2018.
- [28] D. Dowson and G. R. Higginson. *Elasto-hydrodynamic lubrication*. Pergamon Press, 1977.
- [29] C. Barus. Isothermals, isopiestic and isometrics relative to viscosity. *American Journal of Science*, s3-45(266):87–96, 2013.
- [30] P. W. Bridgman. Viscosities to 30,000 kg/cm². *Proceedings of the American Academy of Arts and Sciences*, 77(4):117–128, 1949.
- [31] S. Bair. The unresolved definition of the pressure-viscosity coefficient. *Scientific Reports*, 12(1):1–7, 12 2022.
- [32] S. Bair. Rheology and high-pressure models for quantitative elastohydrodynamics. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 223(4):617–628, 4 2009.
- [33] J. D. Barnett and C. D. Bosco. Viscosity measurements on liquids to pressures of 60 kbar. *Journal of Applied Physics*, 40(8):3144–3150, 7 1969.
- [34] H. E. King, E. Herbolzheimer, and R. L. Cook. The diamond-anvil cell as a high-pressure viscometer. *Journal of Applied Physics*, 71(5):2071–2081, 3 1992.
- [35] S. Bair. Pressure-Viscosity Behavior of Lubricants to 1.4 GPa and Its Relation to EHD Traction. *Tribology Transactions*, 43(1):91–99, 1 2000.
- [36] S. Bair. A routine high-pressure viscometer for accurate measurements to 1 GPa. *Tribology Transactions*, 47(3):356–360, 7 2004.
- [37] C. McCabe, S. Cui, P. T. Cummings, P. A. Gordon, and R. B. Saeger. Examining the rheology of 9-octylheptadecane to giga-pascal pressures. *Journal of Chemical Physics*, 114(4):1887–1891, 1 2001.

- [38] P. Liu, H. Yu, N. Ren, F. E. Lockwood, and Q. J. Wang. Pressure-Viscosity Coefficient of Hydrocarbon Base Oil through Molecular Dynamics Simulations. *Tribology Letters*, 60(3):1–9, 12 2015.
- [39] U. S. Ramasamy, S. Bair, and A. Martini. Predicting Pressure–Viscosity Behavior from Ambient Viscosity and Compressibility: Challenges and Opportunities. *Tribology Letters*, 57(2):11, 2 2015.
- [40] M. A. Galvani Cunha and M. O. Robbins. Determination of pressure-viscosity relation of 2,2,4-trimethylhexane by all-atom molecular dynamics simulations. *Fluid Phase Equilibria*, 495:28–32, 9 2019.
- [41] J. P. Ewen, H. A. Spikes, and D. Dini. Contributions of Molecular Dynamics Simulations to Elastohydrodynamic Lubrication. *Tribology Letters*, 69(1):1–15, 2 2021.
- [42] S. Bair and F. Qureshi. The high pressure rheology of polymer-oil solutions. *Tribology International*, 36(8):637–645, 8 2003.
- [43] C. Mary, D. Philippon, L. Lafarge, D. Laurent, F. Rondelez, S. Bair, and P. Vergne. New insight into the relationship between molecular effects and the rheological behavior of polymer-thickened lubricants under high pressure. *Tribology Letters*, 52(3):357–369, 12 2013.
- [44] H. Spikes. Basics of EHL for practical application. *Lubrication Science*, 27(1):45–67, 1 2015.
- [45] A. W. Crook. The lubrication of rollers IV. Measurements of friction and effective viscosity. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, 255(1056):281–312, 1 1963.
- [46] C. R. Evans and K. L. Johnson. The rheological properties of elastohydrodynamic lubricants. *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, 200(5):303–312, 1986.
- [47] C. R. Evans and K. L. Johnson. Regimes of traction in elastohydrodynamic lubrication. *Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science*, 200(5):313–324, 8 1986.
- [48] K. L. Johnson and J. L. Tevaarwerk. Shear Behaviour of Elastohydrodynamic Oil Films. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 356(1685):215–236, 8 1977.

- [49] F. W. Smith. Lubricant behavior in concentrated contact—some rheological problems. *ASLE Transactions*, 3(1):18–25, 1960.
- [50] S. Bair and W. O. Winer. A Rheological Model for Elastohydrodynamic Contacts Based on Primary Laboratory Data. *Journal of Lubrication Technology*, 101(3):258, 7 1979.
- [51] F. Guo, P. L. Wong, M. Geng, and M. Kaneta. Occurrence of wall slip in elastohydrodynamic lubrication contacts. *Tribology Letters*, 34(2):103–111, 5 2009.
- [52] L. Martinie and P. Vergne. Lubrication at Extreme Conditions: A Discussion About the Limiting Shear Stress Concept. *Tribology Letters*, 63(2):21, 8 2016.
- [53] H. A. Francis. Interfacial temperature distribution within a sliding hertzian contact. *ASLE Transactions*, 14(1):41–54, 1971.
- [54] T. Reddyhoff, A. Schmidt, and H. Spikes. Thermal Conductivity and Flash Temperature. *Tribology Letters*, 67(1):22, 3 2019.
- [55] S. N. Ndiaye, L. Martinie, D. Philippon, N. Devaux, and P. Vergne. A Quantitative Friction-Based Approach of the Limiting Shear Stress Pressure and Temperature Dependence. *Tribology Letters*, 65(4):1–14, 12 2017.
- [56] American Petroleum Institute. API 1509 - Engine Oil Licensing and Certification System. (May):API 1509, 21th edition, February 2022, 2021.
- [57] G. J. Souillard, F. Van Quaethoven, and R. B. Dyer. Polyisobutylene, a new synthetic material for lubrication. In *SAE Technical Papers*. SAE International, 1971.
- [58] M. E. O. G. Hof. Do esters make sense for fluids in electric vehicles? In *STLE 76th Annual Meeting & Exhibition*, 2022.
- [59] J. A. Cecilia, D. B. Plata, R. M. A. Saboya, F. M. T. de Luna, C. L. Cavalcante, and E. Rodríguez-Castellón. An overview of the biolubricant production process: Challenges and future perspectives. *Processes*, 8(3):257, 3 2020.
- [60] ASTM International. ASTM D2270-10(2016) Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40°C and 100°C, 2016.
- [61] H. A. Bruson. US patent - Composition of matter and process, 1937.
- [62] T. W. Selby. The non-newtonian characteristics of lubricating oils. *ASLE Transactions*, 1(1):68–81, 1 1958.

- [63] H. Müller. Mechanism of action of viscosity index improvers. *Tribology International*, 11(3):189–192, 6 1978.
- [64] M. J. Covitch and K. J. Trickett. How Polymers Behave as Viscosity Index Improvers in Lubricating Oils. *Advances in Chemical Engineering and Science*, 05(02):134–151, 3 2015.
- [65] P. Cusseau, N. Bouscharain, L. Martinie, D. Philippon, P. Vergne, and F. Briand. Rheological Considerations on Polymer-Based Engine Lubricants: Viscosity Index Improvers versus Thickeners—Generalized Newtonian Models. *Tribology Transactions*, (October 2017):1–11, 2017.
- [66] Y. Tsunashima, M. Hirata, and Y. Kawamata. Diffusion motions and microphase separation of styrene-butadiene diblock copolymer in solution. 1. extremely dilute solution region. *Macromolecules*, 23(4):1089–1096, 1990.
- [67] M. J. Covitch. How Polymer Architecture Affects Permanent Viscosity Loss of Multigrade Lubricants. In *SAE Technical paper series*, 10 1998.
- [68] L. R. Rudnick. *Lubricant Additives Chemistry and Applications*. CRC Press, 2003.
- [69] A. Martini, U. S. Ramasamy, and M. Len. Review of Viscosity Modifier Lubricant Additives. *Tribology Letters*, 66(2):1–14, 2018.
- [70] J. E. Glass, D. N. Schulz, and C. F. Zukoski. *Polymers as Rheology Modifiers*, volume 462 of *ACS Symposium Series*. American Chemical Society, Washington, DC, 5 1991.
- [71] W. L. Van Horne. Polymethacrylates as Viscosity Index Improvers and Pour Point Depressants. *Industrial and Engineering Chemistry*, 41(5):952–959, 5 1949.
- [72] S. A. Mohamad, N. S. Ahmed, S. M. Hassanein, and A. M. Rashad. Investigation of polyacrylates copolymers as lube oil viscosity index improvers. *Journal of Petroleum Science and Engineering*, 100:173–177, 12 2012.
- [73] C. D. Neveu, R. Sondjaja, T. Stöhr, and N. J. Iroff. *Lubricant and Fuel Additives Based on Polyalkylmethacrylates*, volume 10. Elsevier B.V., 2012.
- [74] L. Cosimbescu, J. W. Robinson, Y. Zhou, and J. Qu. Dual functional star polymers for lubricants. *RSC Advances*, 6(89):86259–86268, 9 2016.
- [75] C. Mary. *Physico-chemistry, high pressure rheology and film-forming capacity of polymer-base oil solutions in EHL*. PhD thesis, 2 2014.

- [76] L. Cosimbescu, J. W. Robinson, and J. P. Page. Polymer Architecture: Does It Influence Shear Stability? *Industrial and Engineering Chemistry Research*, 57(35):11858–11867, 9 2018.
- [77] G. Ver Strate and M. Struglinski. Polymers as lubricating-oil viscosity modifiers. In *ACS Symp. Ser.*, volume 462, pages 256–272. 5 1991.
- [78] M. Smeeth, H. Spikes, and S. Gunsel. Boundary Film Formation by Viscosity Index Improvers. *Tribology Transactions*, 39(3):726–734, 1 1996.
- [79] G. Guangteng, M. Smeeth, P. M. Cann, and H. A. Spikes. Measurement and Modelling of Boundary Film Properties of Polymeric Lubricant Additives. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 210(1):1–15, 3 1996.
- [80] M. Müller, K. Topolovec-Miklozic, A. Dardin, and H. A. Spikes. The Design of Boundary Film-Forming PMA Viscosity Modifiers. *Tribology Transactions*, 49(2):225–232, 7 2006.
- [81] J. Fan, M. Müller, T. Stöhr, and H. A. Spikes. Reduction of friction by functionalised viscosity index improvers. *Tribology Letters*, 28(3):287–298, 12 2007.
- [82] T. A. Gmür, J. Mandal, J. Cayer-Barrio, and N. D. Spencer. Towards a Polymer-Brush-Based Friction Modifier for Oil. *Tribology Letters*, 69(4):124, 12 2021.
- [83] ASTM International. ASTM D5275-17 Standard Test Method for Fuel Injector Shear Stability Test (FISST) for Polymer Containing Fluids, 2017.
- [84] ASTM International. ASTM D6278-17e1 Standard Test Method for Shear Stability of Polymer Containing Fluids Using a European Diesel Injector Apparatus, 2017.
- [85] ASTM International. ASTM D6022-06(2012) Standard Practice for Calculation of Permanent Shear Stability Index, 2012.
- [86] H. H. Horowitz. Predicting Effects of Temperature and Shear Rate on Viscosity of Viscosity Index-Improved Lubricants. *Industrial & Engineering Chemistry*, 50(7):1089–1094, 7 1958.
- [87] R. L. Stambaugh and R. J. Kopko. Behavior of Non-Newtonian Lubricants in High Shear Rate Applications. In *National Automobile Engineering Meeting*, 2 1973.
- [88] P. M. Cann and H. A. Spikes. In lubro studies of lubricants in EHD contacts using FTIR absorption spectroscopy. *Tribology Transactions*, 34(2):248–256, 1991.

- [89] E. C. Lee and S. J. Muller. Flow light scattering studies of polymer coil conformation in solutions under shear: Effect of solvent quality. *Polymer*, 40(10):2501–2510, 5 1999.
- [90] J. F. S. Yu, J. L. Zakin, and G. K. Patterson. Mechanical degradation of high molecular weight polymers in dilute solution. *Journal of Applied Polymer Science*, 23(8):2493–2512, 4 1979.
- [91] P. Ghosh, A. V. Pantar, U. S. Rao, and A. S. Sarma. Shear stability of polymers used as viscosity modifiers in lubricating oils. *Indian Journal of Chemical Technology*, 5(5):309–314, 1998.
- [92] L. G. Wood. The change of viscosity of oils containing high polymers when subjected to high rates of shear. *British Journal of Applied Physics*, 1(8):202–206, 8 1950.
- [93] N. Marx, A. Ponjavic, R. I. Taylor, and H. A. Spikes. Study of Permanent Shear Thinning of VM Polymer Solutions. *Tribology Letters*, 65(3):1–15, 2017.
- [94] N. Marx, L. Fernández, F. Barceló, and H. Spikes. Shear Thinning and Hydrodynamic Friction of Viscosity Modifier-Containing Oils. Part II: Impact of Shear Thinning on Journal Bearing Friction. *Tribology Letters*, 66(3):1–11, 2018.
- [95] H. Spikes and J. Zhang. History, origins and prediction of elastohydrodynamic friction. *Tribology Letters*, pages 56, 1–25, 2014.
- [96] H. Eyring. Viscosity, plasticity, and diffusion as examples of absolute reaction rates. *The Journal of Chemical Physics*, 4(4):283–291, 4 1936.
- [97] P. J. Carreau. Rheological Equations from Molecular Network Theories. *Trans Soc Rheol*, 16(1):99–127, 3 1972.
- [98] M. Rubinstein and R. H. Colby. *Polymer physics*. Oxford University Press, 2003.
- [99] D. E. Smith, H. P. Babcock, and S. Chu. Single-Polymer Dynamics in Steady Shear Flow. *Science*, 283(5408):1724–1727, 1999.
- [100] G. Kraus and J. T. Gruver. Rheological properties of cis-polybutadiene. *Journal of Applied Polymer Science*, 9(2):739–755, 2 1965.
- [101] D. A. Wever, L. M. Polgar, M. C. Stuart, F. Picchioni, and A. A. Broekhuis. Polymer molecular architecture as a tool for controlling the rheological properties of aqueous polyacrylamide solutions for enhanced oil recovery. *Industrial and Engineering Chemistry Research*, 52(47):16993–17005, 11 2013.

- [102] K. Yasuda, R. C. Armstrong, and R. E. Cohen. Shear flow properties of concentrated solutions of linear and star branched polystyrenes. *Rheologica Acta*, 20(2):163–178, 3 1981.
- [103] R. J. A. Eckert. US patent - Hydrogenated star-shaped polymer, 9 1978.
- [104] A. Jabbarzadeh, J. D. Atkinson, and R. I. Tanner. Effect of molecular shape on rheological properties in molecular dynamics simulation of star, H, comb, and linear polymer melts. *Macromolecules*, 36(13):5020–5031, 2003.
- [105] L. I. Kioupis and E. J. Maginn. Molecular Simulation of Poly- α -olefin Synthetic Lubricants: Impact of Molecular Architecture on Performance Properties. *The Journal of Physical Chemistry B*, 103(49):10781–10790, 1999.
- [106] J.-D. Wheeler, P. Vergne, N. Fillot, and D. Philippon. On the relevance of analytical film thickness EHD equations for isothermal point contacts: Qualitative or quantitative predictions? *Friction*, 4(4):369–379, 12 2016.
- [107] B. J. Hamrock and D. Dowson. Isothermal Elastohydrodynamic Lubrication of Point Contacts: Part III-Fully Flooded Result. *Journal of Tribology*, 99(2):264–275, 4 1977.
- [108] R. J. Chittenden, D. Dowson, J. F. Dunn, and C. M. Taylor. A Theoretical Analysis of the Isothermal Elastohydrodynamic Lubrication of Concentrated Contacts. II. General Case, with Lubricant Entrainment along Either Principal Axis of the Hertzian Contact Ellipse or at Some Intermediate Angle. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 397(1813):271–294, 2 1985.
- [109] S. Bair. An experimental verification of the significance of the reciprocal asymptotic isoviscous pressure for EHD lubricants. *Tribology Transactions*, 36(2):153–160, 1993.
- [110] F. J. Westlake and A. Cameron. Fluid film interferometry in lubrication studies. *Nature*, 214(5088):633–634, 1967.
- [111] S. Bair, P. Vergne, and M. Querry. A unified shear-thinning treatment of both film thickness and traction in EHD. *Tribology Letters*, 18(2):145–152, 2 2005.
- [112] L. D. Wedeven, D. Evans, and A. Cameron. Optical analysis of ball bearing starvation. *Journal of Tribology*, 93(3):349–361, 7 1971.

- [113] N. Marx, L. Fernández, F. Barceló, and H. Spikes. Shear Thinning and Hydrodynamic Friction of Viscosity Modifier-Containing Oils. Part I: Shear Thinning Behaviour. *Tribology Letters*, 66(3):1–14, 2018.
- [114] W. Habchi, S. Bair, F. Qureshi, and M. Covitch. A Film Thickness Correction Formula for Double-Newtonian Shear-Thinning in Rolling EHL Circular Contacts. *Tribology Letters*, 50(1):59–66, 4 2013.
- [115] S. Bair and M. Khonsari. An EHD Inlet Zone Analysis Incorporating the Second Newtonian. *Journal of Tribology*, 118(2):341, 4 1996.
- [116] A. Ponjavic and J. S. Wong. The effect of boundary slip on elastohydrodynamic lubrication. *RSC Advances*, 4(40):20821–20829, 5 2014.
- [117] P. Wang and T. Reddyhoff. Wall slip in an EHL contact lubricated with 1-dodecanol. *Tribology International*, 113:197–205, 2017.
- [118] A. Maciel, V. Salas, J. F. A. Soltero, J. Guzmán, and O. Manero. On the wall slip of polymer blends. *Journal of Polymer Science Part B: Polymer Physics*, 40(4):303–316, 2 2002.
- [119] H. A. Barnes. A review of the slip (wall depletion) of polymer solutions, emulsions and particle suspensions in viscometers: its cause, character, and cure. *Journal of Non-Newtonian Fluid Mechanics*, 56(3):221–251, 3 1995.
- [120] R. Pit, H. Hervet, and L. Léger. Friction and slip of a simple liquid at a solid surface. *Tribology Letters*, 7(2-3):147–152, 1999.
- [121] K. Yoshida, K. Hosonuma, and T. Sakurai. Behaviour of polymer-thickened oils in lubricated concentrated contacts. *Wear*, 98(C):63–78, 11 1984.
- [122] R. W. M. Wardle, R. C. Coy, P. M. Cann, and H. A. Spikes. An ‘in lubro’ study of viscosity index improvers in EHD contacts. *Lubrication Science*, 3(1):45–62, 10 1990.
- [123] J. Zhang, A. Tan, and H. Spikes. Effect of Base Oil Structure on Elastohydrodynamic Friction. *Tribology Letters*, 65(1):13, 3 2017.
- [124] H. A. Spikes and P. M. Cann. The development and application of the spacer layer imaging method for measuring lubricant film thickness. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 215(3):261–277, 3 2001.
- [125] H. A. Spikes. Sixty years of EHL. *Lubrication Science*, 18(4):265–291, 10 2006.

- [126] N. A. Marx. *Improving engine efficiency via polymer shear thinning*. PhD thesis, Imperial College London, 2016.
- [127] P. M. Cann, H. A. Spikes, and J. Hutchinson. The development of a spacer layer imaging method (SLIM) for mapping elastohydrodynamic contacts. *Tribology Transactions*, 39(4):915–921, 1 1996.
- [128] S. Bair and W. O. Winer. A new high-pressure, high-shear stress viscometer and results for lubricants. *Tribology Transactions*, 36(4):721–725, 1993.
- [129] S. Bair. The high pressure rheology of some simple model hydrocarbons. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 216(3):139–149, 2002.
- [130] E. W. Merrill. A coaxial cylinder viscometer for the study of fluids under high velocity gradients. *Journal of Colloid Science*, 9(1):7–19, 2 1954.
- [131] P. Dontula, C. W. Macosko, and L. E. Scriven. Does the viscosity of glycerin fall at high shear rates? *Industrial and Engineering Chemistry Research*, 38(4):1729–1735, 1999.
- [132] R. P. Glovnea and H. A. Spikes. Mapping shear stress in elastohydrodynamic contacts. *Tribology Transactions*, 38(4):932–940, 1995.
- [133] V. W. King and J. L. Lauer. Temperature gradients through ehd films and molecular alignment evidenced by infrared spectroscopy. *Journal of Tribology*, 103(1):65–73, 1 1981.
- [134] D. J. Gardiner, E. Baird, A. C. Gorvin, W. E. Marshall, and M. P. Dare-Edwards. Raman spectra of lubricants in elastohydrodynamic entrapments. *Wear*, 91(1):111–114, 10 1983.
- [135] D. J. Gardiner, E. M. Baird, C. Craggs, M. P. Dare-Edwards, and J. C. Bell. Raman microspectroscopy of a working elastohydrodynamic contact. *Lubrication Science*, 1(4):301–313, 7 1989.
- [136] A. M. Williams and D. Ben-Amotz. Molecular-Optical Viscometer Based on Fluorescence Depolarization. *Analytical Chemistry*, 64(6):700–703, 1992.
- [137] S. Bair and W. . Winer. Observations of Shear Localization in Liquid Lubricants Under Pressure. Technical report, 1993.
- [138] T. Reddyhoff, J. H. Choo, H. A. Spikes, and R. P. Glovnea. Lubricant flow in an elastohydrodynamic contact using fluorescence. *Tribology Letters*, 38(3):207–215, 6 2010.

- [139] A. Ponjavic, M. Chennaoui, and J. S. S. Wong. Through-Thickness Velocity Profile Measurements in an Elastohydrodynamic Contact. *Tribology Letters*, 50(2):261–277, 5 2013.
- [140] J. Dench, N. Morgan, and J. S. S. Wong. Quantitative Viscosity Mapping Using Fluorescence Lifetime Measurements. *Tribology Letters*, 65(1):25, 3 2017.
- [141] J. Dench. *Comparing the global and molecular rheology of fluids, in situ, under high pressures*. PhD thesis, Imperial College London, 2018.
- [142] ThermoFisher. Fluorescence SpectraViewer.
- [143] W. Akers and M. A. Haidekker. A molecular rotor as viscosity sensor in aqueous colloid solutions. *Journal of Biomechanical Engineering*, 126(3):340–345, 6 2004.
- [144] N. Amdursky, R. Gepshtein, Y. Erez, N. Koifman, and D. Huppert. Pressure effect on the nonradiative process of thioflavin-T. *Journal of Physical Chemistry A*, 115(24):6481–6487, 6 2011.
- [145] J. R. Lakowicz. *Principles of fluorescence spectroscopy*. Springer, 2006.
- [146] J. H. Choo, R. P. Glovnea, A. K. Forrest, and H. A. Spikes. A low friction bearing based on liquid slip at the wall. *Journal of Tribology*, 129(3):611–620, 7 2007.
- [147] N. Fillot, H. Berro, and P. Vergne. From continuous to molecular scale in modelling elastohydrodynamic lubrication: Nanoscale surface slip effects on film thickness and friction. *Tribology Letters*, 43(3):257–266, 9 2011.
- [148] D. Savio, N. Fillot, P. Vergne, H. Hetzler, W. Seemann, and G. E. Morales Espejel. A multiscale study on the wall slip effect in a ceramic-steel contact with nanometer-thick lubricant film by a nano-to-elastohydrodynamic lubrication approach. *Journal of Tribology*, 137(3), 7 2015.
- [149] A. Cuenca and H. Bodiguel. Submicron flow of polymer solutions: Slippage reduction due to confinement. *Physical Review Letters*, 110(10):108304, 3 2013.
- [150] G. Guyard, A. Vilquin, N. Sanson, S. Jouenne, F. Restagno, and J. D. McGraw. Near-surface rheology and hydrodynamic boundary condition of semi-dilute polymer solutions. *Soft Matter*, 17(14):3765–3774, 4 2021.
- [151] D. C. Tretheway and C. D. Meinhart. Apparent fluid slip at hydrophobic microchannel walls. *Physics of Fluids*, 14(3):L9–L12, 3 2002.
- [152] P. Joseph and P. Tabeling. Direct measurement of the apparent slip length. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics*, 71(3):035303, 3 2005.

- [153] P. E. Boukany and S. Q. Wang. Exploring the transition from wall slip to bulk shearing banding in well-entangled DNA solutions. *Soft Matter*, 5(4):780–789, 2 2009.
- [154] J. Plucinski, R. K. Gupta, and S. Chakrabarti. Wall slip of mayonnaises in viscometers. *Rheologica Acta*, 37(3):256–269, 6 1998.
- [155] H. Spikes. Friction Modifier Additives. *Tribology Letters*, 60(1):5, 10 2015.
- [156] J. Fan, M. Müller, T. Stöhr, and H. A. Spikes. Reduction of friction by functionalised viscosity index improvers. *Tribology Letters*, 28(3):287–298, 12 2007.
- [157] J. R. Lakowicz, editor. *Principles of Fluorescence Spectroscopy*. Springer US, Boston, MA, 2006.
- [158] M. E. Diaz-Garcia and M. Roza-Fernandez. Room temperature phosphorescent sensing probe for detection of DNA. In N. I. Croitoru, M. Miyagi, G. Orellana, A. Verga Scheggi, and H. J. C. M. Sterenborg, editors, *Medical and Fiber Optic Sensors and Delivery Systems*, volume 2631, pages 29–36. SPIE, 1 1995.
- [159] T. Husberg, S. Gjirja, I. Denbratt, A. Omrane, M. Aldén, and J. Engström. Piston temperature measurement by use of thermographic phosphors and thermocouples in a heavy-duty diesel engine run under partly premixed conditions. In *SAE Technical Papers*. SAE International, 2005.
- [160] J. Holtzinger. *Influence of viscosity modifiers on hydrodynamic friction*. PhD thesis, 2011.
- [161] C. C. Hua and M. S. Wu. Viscometric properties of dilute polystyrene/dioctyl phthalate solutions. *Journal of Polymer Science Part B: Polymer Physics*, 44(5):787–794, 3 2006.
- [162] T. Kume, T. Hashimoto, T. Takahashi, and G. G. Fuller. Rheo-optical studies of shear-induced structures in semidilute polystyrene solutions. *Macromolecules*, 30(23):7232–7236, 11 1997.
- [163] M. Grzelka, I. Antoniuk, Drockenmuller, A. Chennevière, L. Léger, and F. Restagno. Slip and Friction Mechanisms at Polymer Semi-Dilute Solutions/Solid Interfaces. *Macromolecules*, 54(10):4910–4917, 5 2021.
- [164] A. Z. Akcasu and C. C. Han. Molecular Weight and Temperature Dependence of Polymer Dimensions in Solution. *Macromolecules*, 12(2):276–280, 1979.

- [165] K. Huber, S. Bantle, P. Lutz, and W. Burchard. Hydrodynamic and Thermodynamic Behavior of Short-Chain Polystyrene in Toluene and Cyclohexane at 34.5 °C. *Macromolecules*, 18(7):1461–1467, 1985.
- [166] Y. Tsunashima. Polymer chain dynamics in dilute solutions under Couette flow: Dynamic light scattering from polystyrenes in a good solvent. *The Journal of Chemical Physics*, 102(11):4673–4682, 3 1995.
- [167] J. Krim. Friction and energy dissipation mechanisms in adsorbed molecules and molecularly thin films. *Advances in Physics*, 61(3):155–323, 6 2012.
- [168] T. D. Blake. Slip between a liquid and a solid: D.M. Tolstoi’s (1952) theory reconsidered. *Colloids and Surfaces*, 47(C):135–145, 1 1990.
- [169] J. P. Ewen, S. K. Kannam, B. D. Todd, and D. Dini. Slip of Alkanes Confined between Surfactant Monolayers Adsorbed on Solid Surfaces. *Langmuir*, 34(13):3864–3873, 4 2018.
- [170] J. P. Ewen, C. Gattinoni, N. Morgan, H. A. Spikes, and D. Dini. Nonequilibrium Molecular Dynamics Simulations of Organic Friction Modifiers Adsorbed on Iron Oxide Surfaces. 2016.
- [171] H. Mitsui and H. A. Spikes. Predicting EHD Film Thickness of Lubricant Polymer Solutions. *Tribology Transactions*, 41(1):1–10, 1 1998.
- [172] R. J. Chittenden, D. Dowson, J. F. Dunn, and C. M. Taylor. A theoretical analysis of the isothermal elastohydrodynamic lubrication of concentrated contacts. I. Direction of lubricant entrainment coincident with the major axis of the Hertzian contact ellipse. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences*, 397(1813):245–269, 2 1985.
- [173] Y. H. Wang, S. Zheng, W. M. Yang, R. Y. Zhou, Q. F. He, P. Radjenovic, J. C. Dong, S. Li, J. Zheng, Z. L. Yang, G. Attard, F. Pan, Z. Q. Tian, and J. F. Li. In situ Raman spectroscopy reveals the structure and dissociation of interfacial water. *Nature*, 600(7887):81–85, 12 2021.
- [174] C. E. Garcia, M. Ueda, H. Spikes, and J. S. Wong. Temperature dependence of molybdenum dialkyl dithiocarbamate (MoDTC) tribofilms via time-resolved Raman spectroscopy. *Scientific Reports*, 11(1):1–13, 12 2021.
- [175] P. I. Richardson, H. Muhamadali, D. I. Ellis, and R. Goodacre. Rapid quantification of the adulteration of fresh coconut water by dilution and sugars using Raman spectroscopy and chemometrics. *Food Chemistry*, 272:157–164, 1 2019.

- [176] A. Ponjavic, J. Dench, N. Morgan, and J. S. S. Wong. In situ viscosity measurement of confined liquids. *RSC Advances*, 5(121):99585–99593, 11 2015.
- [177] J. A. Levitt, P. Chung, M. K. Kuimova, G. Yahiolu, Y. Wang, J. Qu, and K. Suhling. Fluorescence Anisotropy of Molecular Rotors. *ChemPhysChem*, 12(3):662–672, 2 2011.
- [178] A. Vyšniauskas, M. Qurashi, N. Gallop, M. Balaz, H. L. Anderson, and M. K. Kuimova. Unravelling the effect of temperature on viscosity-sensitive fluorescent molecular rotors. *Chemical Science*, 6(10):5773–5778, 9 2015.
- [179] S. Bair and W. O. Winer. The Pressure-Viscosity Coefficient at Hertz Pressure And Its Relation To Concentrated Contact Traction. *Tribology Series*, 38:433–443, 1 2000.
- [180] S. Bair. The viscosity at the glass transition of a liquid lubricant. *Friction*, 7(1):86–91, 2 2019.
- [181] W. Habchi, P. Vergne, S. Bair, O. Andersson, D. Eyheramendy, and G. Morales-Espejel. Influence of pressure and temperature dependence of thermal properties of a lubricant on the behaviour of circular TEHD contacts. *Tribology International*, 43(10):1842–1850, 10 2010.
- [182] M. Björling, W. Habchi, S. Bair, R. Larsson, and P. Marklund. Towards the true prediction of EHL friction. *Tribology International*, 66:19–26, 10 2013.
- [183] W. Habchi, S. Bair, and P. Vergne. On friction regimes in quantitative elastohydrodynamics. *Tribology International*, 58:107–117, 2 2013.
- [184] Y. Liu, Q. J. Wang, S. Bair, and P. Vergne. A Quantitative Solution for the Full Shear-Thinning EHL Point Contact Problem Including Traction. *Tribology Letters*, 28(2):171–181, 9 2007.
- [185] S. Bair, C. McCabe, and P. T. Cummings. Calculation of Viscous EHL Traction for Squalane Using Molecular Simulation and Rheometry. *Tribology Letters*, 13(4):251–254, 2002.
- [186] E. Ciulli, K. Stadler, and T. Draexl. The influence of the slide-to-roll ratio on the friction coefficient and film thickness of EHD point contacts under steady state and transient conditions. *Tribology International*, 42(4):526–534, 4 2009.
- [187] A. W. Crook. The lubrication of rollers III. A theoretical discussion of friction and the temperatures in the oil film. *Philosophical Transactions of the Royal Society*

- of London. *Series A, Mathematical and Physical Sciences*, 254(1040):237–258, 12 1961.
- [188] J. Archard. The temperature of rubbing surfaces. *Wear*, 2(6):438–455, 10 1959.
- [189] R. Larsson and O. Andersson. Lubricant thermal conductivity and heat capacity under high pressure. *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 214(4):337–342, 4 2000.
- [190] J. C. Jaeger. Moving sources of heat and the temperature at sliding contacts. *Journal and Proceedings of The Royal Society of New South Wales*, 75-76:203–224, 1942.
- [191] A. V. Olver. Testing Transmission Lubricants: The Importance of Thermal Response. *Proceedings of the Institution of Mechanical Engineers, Part G: Journal of Aerospace Engineering*, 205(1):35–44, 1 1991.
- [192] S. Bair. Is it possible to extract the pressure dependence of low-shear viscosity from EHL friction? Revised May, 2020. *Tribology International*, 151:106454, 11 2020.
- [193] J. Filik. Raman Spectroscopy: A Simple, Non-Destructive way to Characterise Diamond and Diamond-Like Materials. *Spectroscopy Europe*, 17(5):10–17, 2005.