MICRORHEOMETRY FOR STUDYING THE RHEOLOGY AND DYNAMICS OF POLYMERS NEAR INTERFACES

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The design of an instrument capable of opto-mechanical studies of the rheology of viscoelastic polymeric fluids near solid interfaces is described. The instrument probes the 'meso'-scale (length scales of o (μm)) and bridges the gap between molecular-scale devices such as the Surface Force Apparatus (SFA) and conventional rheometers. The high viscosity materials and intermediate length scales probed with the current device are of direct relevance to industrial coating and thin film polymer processing operations, in addition to fundamental investigations of slip and interfacial instabilities. The device utilises small fluid samples (of the order of 1 μL), allows a wide range of viscosities (and thus molecular weights) to be investigated and can also be used with different substrate materials and surface coatings. Direct optical access to the sample also permits in-situ rheo-optical studies of material response under different loading conditions and flow histories.

1 INTRODUCTION

The conformational and dynamical behaviour of polymers near surfaces is of vital interest to the polymer processing industry. Problems associated with extrusion and film processing and fundamental studies of adhesion or the understanding of new biochemical systems all require a need to develop a clear picture of how macromolecules behave near interfaces. Of particular interest are the behaviour of polymer melts as they are processed under strong shearing conditions and the onset of viscoelastic flow instabilities. These instabilities lead to unstable flow and extrudate distortion which have been attributed (at least in part) to the violation of the no-slip condition at the polymer-metal interface [1, 2]. We do not pursue a detailed review of these phenomena; however we note that there is still considerable discussion in the literature over the mechanism and cause of these effects [2-7].

The physical models for these phenomena typically invoke molecular, or micro-mechanical, arguments. The resulting failure modes predicted by these models vary considerably, and lead to unstable motions with markedly different spatial and temporal characteristics. For example, in support of evidence for a critical stress-induced slip (predicted by most bulk techniques such as capillary rheometry [3, 8, 9]), various authors have argued that a cohesive failure is the most likely mechanism [9, 10]. Here, chain disentanglement occurs between the adsorbed layer and the bulk, and hence the slip plane is close to, but not at, the interface. However, a recent study by Mackay and Henson suggests that slippage can occur at any stress and the authors argue that a critical stress is more likely to be a result of sensitivity limitations when attempting to measure these small stresses using a conventional bulk technique. Forcible desorption of the entangled polymers from the surface due to the externally imposed flow (effectively an adhesive failure) has also been blamed for apparent wall slip [12]. Significantly, both explanations predict that the dynamics of such events are connected to the conformational changes induced in the layer of molecules adjacent to the substrate. The polymer chains nearest the wall are expected to have markedly different relaxation times (and hence effective viscosities) from the entangled macromolecules in the bulk melt [13]. This effect is increasingly important as the molecular weight and degree of entanglement of the chains increases [14]. It is therefore of both practical and theoretical interest to examine the non-equilibrium behavior of high molecular weight polymer chains at solid-melt interfaces, and the associated dynamical slip or 'stick-slip' events that are involved in the development of 'sharkskin' and, eventually, gross melt fracture [15]. It is worth emphasising that these conformational changes will also affect the linear viscoelastic properties of the system [13]. However, experimental investigations of slip at small strain amplitudes are extremely limited and most slip studies to date have focussed on steady shear or large amplitude oscillatory behaviour.

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scales. We have outlined the design considerations and construction issues faced in building a microrheometer. We have emphasised the problems associated with the requirement for parallelism and the necessity for an absolute measure of the gap. We have also clearly demonstrated that these problems are solvable and allow the design of a parallel plate rheometer capable of operating at very small separations. In the present configuration, the instrument is driven electromagnetically, allowing us to keep the lateral compliance within reasonable limits. Strain is derived from an inductive position sensor and, by adjusting the stiffness of the leaf springs, a broad range of fluid properties can be accessed. From the data presented we show that the apparatus is capable of probing rheological properties down to gaps of less than ten microns. In addition the device can also be used as a conventional rheometer for unusual, rare, or expensive materials in which large samples are not available. The use of interferometry provides an absolute measure of the gap and the parallelism and hence removes any uncertainty about gap variations during the course of an experiment. Conversely a measurement of normal displacement during imposed shearing deformation could be used to obtain the normal force exerted by the fluid during the deformation (if the vertical compliance is calibrated). We plan to report on such enhancements in the future. Also the instrument has been designed with the specific intention of supporting higher sample temperatures and leaving the sample optically accessible for opto-rheological experiments. Current research activities in our laboratory include a detailed investigation of the change in apparent viscosity in an homologous series of polymer melts as the gap is varied. We are also investigating the effects of various surface finishes and chemistry (*e.g.* fluorocarbon sprays, roughness, silanisation) on the rheological behaviour of the confined film.

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BIOGRAPHIES

Dr. Gavin J.C. Braithwaite was born in 1970 in Dundee, Scotland. He studied for his B.Sc. in Physics at the University of Edinburgh. After a M.Sc. in Electronics at Southampton University he obtained his doctorate in Chemical Engineering from Imperial College of Science, Technology and Medicine, London working on using AFM type approaches to measure Colloidal Forces. Since then he has been employed as a Research Associate at M.I.T.

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