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Controlling thin liquid film viscosity via modification of substrate surface chemistry

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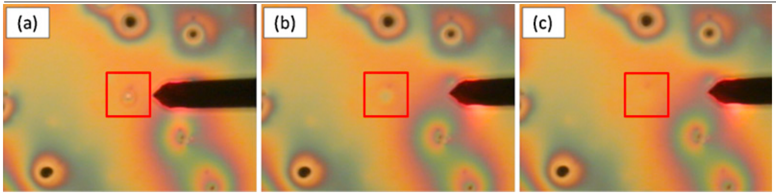
HIGHLIGHTS

- Thin films of spin-deposited silicone fluids.
- Silicon and fluoropolymer-coated silicon substrates.
- Perturbation applied to film using colloid probe atomic force microscopy.
- Film viscosity estimated from time required for recovery of the perturbation.
- Thin film viscosities can be controlled via selection of substrate surface chemistry.

GRAPHICAL ABSTRACT



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ABSTRACT

The viscosity of thin films of liquid poly(dimethylsiloxane) have been studied on silicon and fluoropolymer-coated silicon by means of a perturbation technique applied using colloid probe atomic force microscopy. The liquid film supported by a silicon substrate exhibited a greater viscosity than the bulk liquid, due to the strong interaction between the molecules near to the liquid/solid interface. In comparison, the liquid film supported by a fluoropolymer-coated substrate exhibited a similar viscosity to the bulk liquid, due to the weak interaction between the liquid and the fluoropolymer surface. This demonstrates the possibility to control the viscosity of thin liquid films via selection of the substrate chemical properties.

1. Introduction

Thin film structure and dynamics are topics of significant research interest, with applications in fields as diverse as electronics, healthcare technologies and biomedical engineering. It is well-established that the properties of ultrathin films can vary as a function of the film thickness [1–4] with polymer chain segments at the film/substrate interface exhibiting decreased mobility compared with the bulk film, whereas segments at the free surface exhibit greater mobility than the bulk film. The effect of this anisotropy affects the properties of materials which include viscosity [1], glass transition temperatures [2–3], diffusion coefficients [4], and rheological properties [5]. For systems where there was a favourable interaction between the film and the surface chemical moieties of the supporting substrate, the properties of the film differed from those of the bulk. Granick and co-workers have employed techniques such as the surface forces apparatus and extensively studied the properties of polymer melts, show-

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ing that geometric confinement reduces polymer chain mobility regardless of the presence or absence of favourable intermolecular interactions [6–8]. In cases where extreme confinement of molecules is conferred, liquid films were made to behave as if they were solids [9–10]. Similarly, researchers such as Ducker [11] and Butt [12] have used atomic force microscopy to study the lubrication behaviour, slip properties, and interfacial molecular organisation of thin liquid polymer films. Butt and co-workers have also studied the propensity of molecules to form brush-like layers at the solid/liquid interface, due to the end groups present in the molecular chains [13].

In this work, we present a simple model for assessing the viscosity of thin liquid films, and investigate the viscosities of films deposited onto different surfaces which the bulk liquid wets favourably and unfavourably. Thin films of liquid poly(dimethylsiloxane) (PDMS) were spin-cast onto silicon and fluoropolymer-coated silicon substrates. The viscosities of the liquid PDMS films were assessed via video microscopy by applying a perturbation to the surface of the film using colloid probe atomic force microscopy, and recording the time required for the surface tension-driven recovery of the perturbation. The film viscosity was calculated using an analytical solution based on a solution originally derived by Middleman [14].

2. Experimental

2.1. Rheometry

The rheological properties of a linear PDMS liquid of zero-shear rate viscosity 30 Pa s (Dow Corning, UK) were measured as a function of shear rate using an AR-G2 rheometer (TA Instruments, UK) with a cone and plate configuration, employing a 40 mm diameter, 2° stainless steel cone. Measurements were performed at a temperature of 20 °C. The molecular weight of the PDMS is approximately 80 kg/mol, which is in excess of the 34 kg/mol critical entanglement molecular weight for PDMS [15]. The radius of gyration of the PDMS is approximately 18 nm, according to the relationship reported by Silberzan and Leger [16] and Valignat et al. [17]. Fig. 1 shows the measured properties, in which it can be seen that the PDMS has a constant viscosity at shear rates $<50\,s^{-1}$; this is the upper Newtonian plateau. At shear rates $>50\,s^{-1}$ the liquid undergoes shear thinning, with the lower Newtonian plateau occurring at shear rates $>10^3\,s^{-1}$.

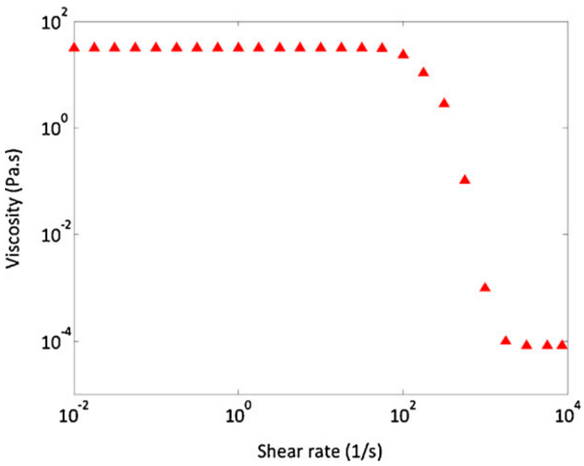

Fig. 1. Viscosity of PDMS liquid as a function of shear rate using cone and plate rheometry

2.2. Preparation of CF_xO_y films

Solid CF_xO_y films were deposited by plasma polymerisation onto the polished side of single crystal N-type Si (100) wafers (IDB Technologies, UK) using a STS Multiplex ICP DRIE etcher (STS Plc., UK), utilising C_4F_8 gas (Pelchem, South Africa) at a flow rate of 80 sccm. The platen power was set to 600 W and the deposition time was 60 s. Wafers were used as received, with any visible dust or debris being removed by sweeping the surface with N_2 gas.

2.3. Preparation of PDMS films

PDMS liquid of 30 Pa s zero-shear rate viscosity was dissolved in HPLC grade toluene (Fisher Scientific, UK) at a concentration of 2% (*w*/*w*). The solution was allowed to equilibrate for 48 h to ensure complete dissolution. A 50 μL droplet of solution was dispensed using a fixed needle syringe (Hamilton, UK) onto the substrate of interest, immediately prior to spin coating (WS-400E-6NPP-Lite, Laurell Technologies, USA), yielding a thin film of PDMS liquid following evaporation of the solvent. The first type of substrates was a clean Si wafer with a 2 nm native SiO_2 surface oxide layer, which is hereafter referred to a Si/SiO_2. The second type of substrate was a solid CF_xO_y film deposited on a clean Si/SiO_2 wafer, which is hereafter referred to as the CF_xO_y film.

2.4. Characterisation of Si surface and CF_xO_y film surface

The thickness of PDMS liquid films and CF_xO_y films was measured using a UVISEL ellipsometer (Jobin-Yvon/Horiba, UK) over the wavelength range 250–800 nm and at an angle of incidence of 70°. Calculation of the film thickness was performed for each measurement, based on a four-phase ambient/CF_xO_y film/SiO_2/Si model, or a five phase ambient/PDMS/CF_xO_y film/SiO_2/Si model in which each layer was assumed to be isotropic. The roughness of the Si surface and CF_xO_y film surface was measured using a NanoWizard II atomic force microscope (AFM, JPK, UK) operating in Intermittent Contact Mode under ambient conditions, employing rectangular pyramidal-tipped Si cantilevers (RTESP, Veeco, UK) with a nominal tip diameter of 50 nm. Extensive details regarding the characterisation of CF_xO_y thin films have previously been described by Cheneler et al. [18]. CF_xO_y films deposited on Si substrates were found to exhibit similar surface roughnesses to the underlying substrate, with R_a values of the order 1 nm.

2.5. Contact angle measurement

The contact angle behaviour of a droplet of PDMS liquid on the Si surface and CF_xO_y film surface was measured using a purpose-built apparatus employing a charge-coupled device (CCD) KP-M1E/K camera (Hitachi, UK) and FTA Video Analysis software v2.0 (First Ten Angstroms, UK).

2.6. Film perturbation

An indentation was made in PDMS liquid films deposited onto the Si surface and CF_xO_y film surface using a rectangular Si cantilever with an attached spherical SiO_2 colloid probe, radius 6 μm, at its apex (NovaScan, USA). A compressive load of 300 nN was applied to the film for approximately 5 s before rapid retraction of the probe. The cantilever spring constant was 20.1 N/m and was calibrated according to the method described by Bowen et al. [19]. The cantilever was housed in a MultiMode AFM (Veeco, UK) operating an ‘E’ scanner, and images were recorded from the white light video system built into the AFM using an analog-to-digital USB video converter (BRSL, UK). Images of the film were captured every 30 s. The recovery of the perturbation was monitored over a period of 2 h