SPREADING OF MICROFILMS AND NANOFILMS OF POLYMER LIQUIDS

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Abstract: Nanotechnology can have a key role in future space flights. Research activities now are focused on the ability to engineer nanostructures with controlled composition, shape and size. We have studied the spreading of polymer liquids (melts) over flat surfaces. Two geometries are considered: horizontal with moving contact line (done by others), and vertical with static contact line (subject of our experiments). In all cases we have found that there are polymer nanofilms spreading ahead from the macroscopic fluid meniscus. The structure of these nanofilms does not seem to depend on the viscosity of the polymer melt, or the experimental conditions (temperature and humidity). Between the nanofilms and the bulk meniscus there are transitional microfilms, which seem to be controlled by the van der Waals forces. The speed of spreading of both micro and nano films seems to depend strongly on the viscosity of the polymer melt..

РАЗПРОСТРАНЕНИЕ НА МИКРО- И НАНОСЛОЕВЕ НА ПОЛИМЕРНИ ТЕЧНОСТИ

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Резюме: Нанотехнологиите се предвижда да играят ключова роля в бъдещи космически полети. Научноизследователските усилия сега са фокусирани върху способността ни да създаваме наноструктури със контролиран състав, форма и размер. В тази статия ние разглеждаме разпространението на тънки слоеве от полимерни течности върху равни повърхности. Две геометрии са разгледани: хоризонтална с движеща се линия на контакт (експерименти и симулации извършени от други учени), и вертикална със статична линия на контакт (обект на нашите експерименти). Във всички случаи ние открихме наличието на полимерни нанослоеве, разпространяващи пред макроскопичния менискус на полимерната течност. Структурата на тези нанослоеве изглежда не зависи от вискозитета на полимерната течност, или експерименталните условия (температура или влажност). Между нанослоевете и мениска се намират преходни полимерни микрослоеве, които изглежда се контролират от Ван дер Ваалсови сили. Скоростта на разпространение на микро- и нанослоевете зависи силно от вискозитета на полимерната течност.

Introduction

We have studied a cascade of structures connecting the bulk meniscus on a vertical plate (millimeter to micron thicknesses), through Van der Waals (~100 A thick) and molecular scale (~10 A thick) films,

to the bare surface. Our measurements have used small beam X-ray reflectivity to probe molecular to micron scales and geometric beam blocking measurements for thicker films and the bulk meniscus. We have measured and compared two methyl terminated polydimethylsiloxane (PDMS) polymers with viscosities that differ by a factor of one hundred as they contact the silicon oxide layer on bulk silicon crystals.

Recent theoretical and experimental work has been devoted to the structure of precursing films of the same polymer melt we employ (polydimethylsiloxane) moving ahead of the meniscus of a spreading drop. Many of the recent experiments in this area were done by the group of A. M. Cazabat

[1, 2, 3, 4, 5, 6, 7] in France. They measured how the size and thickness of a spreading drop evolves with time on different surfaces, and at different humidities. Their measurements were done by using optical ellipsometry. They found that at suffciently short times (when the drop acts as reservoir for the spreading film) the size of the drop is proportional to √t , where t is the time since the beginning of the spreading. They also found that the structure of the precursing film depends on the surface energy and humidity. They reported that at low humidity (less than 30% RH) the precursing film was a monolayer (thickness 7 A, which is close to the diameter of a PDMS monomer), and at higher humidities theobserved structure was a bilayer (thickness 14 A).

In another series of papers, [7, 8, 9, 10] molecular dynamics (MD) have been used to simulate the situation in the experiments from the Cazabat group. The results from the MD simulations generally confirm the results from the optical ellipsometry experiments: The diameter of the drop is proportional to √t , the spreading is fastest at some intermediate strength of the interaction, and there is a thin precursor layer of polymer molecules diffusing ahead of the contact line. These experiments and simulations measured only the thickness of the spreading film, but they could not reveal its structure. By using X-ray reflectivity, we could not only measure the thickness of the spreading films, but also reveal their structure.

Theory

After a vertical surface touches the polymer liquid, a meniscus is formed. The line where this meniscus touches the solid surface of the silicon crystal is called "contact line". This meniscus is with bigger contact angle, and slowly relaxes to its equilibrium contact angle. According to the Joanny – De Gennes scaling model, [1] the following events take place:

Soon after the formation of the meniscus thick ("adiabatic") film of polymer molecules starts to creep up. The thickness of this film generally is inversely proportional to the distance from the contact line. After some more time thin ("diffusive") film of polymer molecules starts to appear ahead of the thick film. In the crossover region from the thick to the thin film the film thickness is inversely proportional to the square of the distance to the contact line. Later, the thick film reaches its equilibrium (Van der Waals) thickness, and now its thickness is constant, and does not depend on the height, and the film just slowly creeps up. Some time later, the Van der Waals film reaches distance of one capillary length. Finally, the contact angle reaches its equilibrium value.

Method and Experimental Setup

We use specular X-ray reflectivity, [11] which means that we measure the reflected intensity as a function of the incident angle (for specular reflectivity the angle of reflection is equal to the incident angle) of an narrow and well collimated X-ray beam. This reflected intensity besides the angle of incidence depends also on the structure of the reflecting surface. We plot the ratio of the reflected to the incident intensity of the X-ray beam as a function of the incident angle, and we get a so called "reflectivity curve". We then use a fitting program to get from this reflectivity curve the parameters of the reflecting surface, including the parameters of the polymer layer that cover that surface.

Our experimental setup consists of vertically mounted silicon crystal, with its lower end dipped into teflon dish filled with PDMS. This setup can be translated horizontally and vertically, and it can be rotated around vertical axis. The dish is mounted with four screws onto a vertical translation, which allows us to lift the dish (when it is filled with PDMS) until the crystal wafer is dipped into the fluid. The entire experimental stage was covered by a sealed metal chamber with Kapton windows on two opposite sides allowing the X-rays can pass through the chamber. The humidity inside the chamber can be controlled by using helium or beakers with water. We used PDMS with two different viscosities: 10 cSt and 1000 cSt.   For our experiments we used clean rectangular one side polished optically flat Si crystals, 10 cm x 5 cm x 0.5 cm.

Results

We have observed thick Van der Waals film for the 10 cSt PDMS, but not for 1000 cSt PDMS, due to its slow growth in the second case. The graph of the thickness of the Van der Waals film versus height above the contact line is given on fig. 1 . As can be seen from it, the thickness of the Van der Waals film is about 500 A, it is nearly homogeneous, and it can reach up to a centimeter above the contact line for a day after the meniscus is formed.
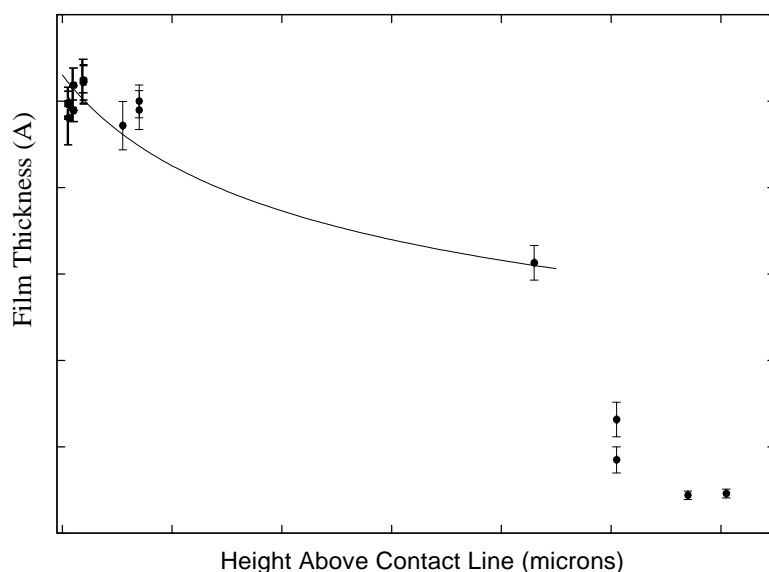
Fig. 1. Thickness vs height for 10 cSt PDMS with fit to for the Van der Waals film. Data - filled circles, fit - solid line

For the high viscosity liquid (1000 cSt PDMS) we have observed also the quasi-static region from the thick to the ultrathin film. The graph of this region is given on fig. 2. This region seems independent from the macroscopic geometry and humidity of the experiment. The thickness of the film there seems to obey a law from the Joanny – De Genes model (i.e., the thickness there is inversely proportional to the square of the distance to the contact line).
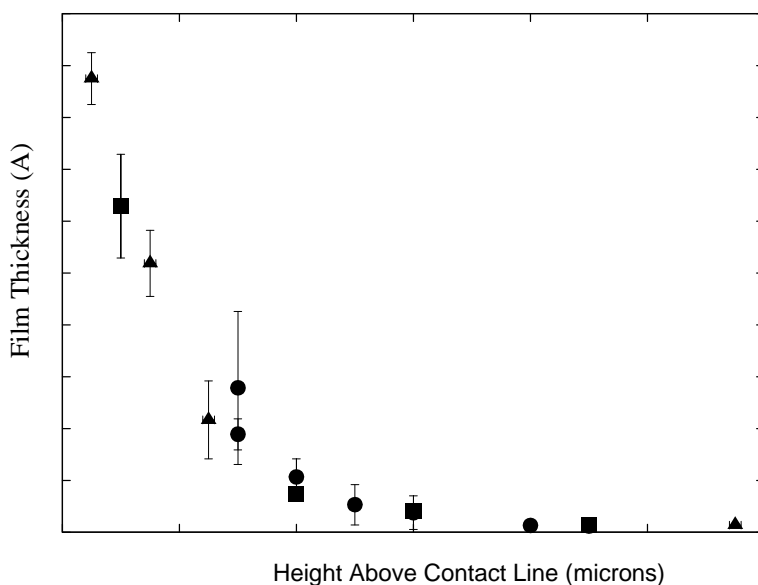

Fig. 2. Comparison of crossover regions between the ultrathin film and the meniscus, in the dry advance case and the end of the hydrodynamic film in the film draining case. Dry advance - filled circles, draining film - filled squares, wet advance - filled triangles

We have observed ultrathin precursing films in all of our experiments. The reflectivity curves of those ultrathin films looked practically identical (but different from the reflectivity scan of the clean crystal high above the meniscus). The structure of the ultrathin film does not seem to depend on the geometry, height, humidity or chain length.

From our fits we have plotted the index of refraction of the X-rays for the thin film (which is proportional to the electron density). From it we concluded, that the ultrathin film extends with decreasing density up to 5 or 6 monomer diameters from the solid surface. This suggests that this ultrathin film consist of entangled polymer chains lying on the solid surface.

Conclusions

- Some aspects of Joanny – De Gennes scaling model confirmed
- Van der Waals film observed
- Quasi-static crossover region from meniscus to ultrathin film observed. Shape of this region independent of macroscopic geometry, or humidity.
- Ultrathin film observed in all experiments. Structure of this film independent of macroscopic geometry, vertical position, humidity or chain length.
- Ultrathin film consists of entangled polymer chains, and extends with decreasing density up to five or six monomer diameters from the surface

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