

PhD fellowship application

GLASS TRANSITION TEMPERATURE AND STABILITY OF THIN POLYMER FILMS: ROLE OF THE INTERFACES

Project description

Miniaturization being a sought after criteria, a large body of work has been devoted over the last twenty years on confinement effects in polymer thin films. Besides the well-known deviation of the glass transition temperature,¹ T_g with respect to the bulk value, polymer thin films in a confined state (thickness < 100 nm) show up many peculiar properties in their viscosity,² physical aging³, and density⁴⁻⁵, compared to their bulk counterpart. In spite of a wealth of experimental and theoretical studies on this topic, there is still an intense controversy over the role played by interfaces on the occurrence of T_g . We have recently shown that by performing Atomic Force Microscopy measurements of pull-off force measurement as a function of the temperature, we were able to probe the dynamic of supported polystyrene (PS) thin films.⁶ We demonstrated the existence of two transition temperatures that can be associated to the relaxation of polymer chains located at different depth regions within the polymer film. Independently of the film thickness, we have confirmed the presence of a region of high mobility for the polymer chains at the free interface. We claim here that our results demonstrate, in agreement with other techniques such as multiwavelength ellipsometry and x-ray reflectivity, the stratification of thin polymer film depth profile in term of relaxation behavior.

In this thesis, using the same methodology we want to study the effect of the interfaces on the polymer chains dynamics. At first the influence of the air/polymer interface will be studied. First results have shown an evolution of i-PMMA chains dynamics as function of the environment humidity. These results will be confirmed. Then the influence of the polymer/substrate nature will be investigated. For this we will use a methodology developed in our team allowing to prepare and characterize stable flat polystyrene films with a controlled thickness ranging from 1.3 nm to 7.0 nm.⁷ Some controversy also exists on the influence of polymer chains length. A part of the project will consist in preparing thin PS films with different Mw. Then chain dynamics will be studied to see if chain entanglement plays a role in the measurement of T_g for thin films. In parallel a theoretical study will be performed to fully understand the AFM pull-off force measurement in terms of probed depth (through the study of controlled thickness bilayers) and mechanical model (with the help of FE modeling).

Keywords

Atomic Force Microscopy (AFM) – Elaboration and characterization of polymer thin films (Xray reflectivity, Ellipsometry)

Candidates required skills

- Strong attention to detail
- Ability to prepare samples cautiously
- Strong analytical and communication skills
- Master in physics, chemistry or material science

Supervisors

The candidate will be based in Le Mans (IMMM) but experimental campaigns will be conducted in Lorient (IRDL)

- Nicolas DELORME (Professor – IMMM): Nicolas.delorme@univ-lemans.fr
- Guillaume VIGNAUD (Ass. Professor – IRDL – Lorient)
- Alain GIBAUD (Professor – IMMM)

References

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- ⁶ N. Delorme, M. S. Chebil, G. Vignaud, V. Le Houerou, J. F. Bardeau, R. Busselez, A. Gibaud, and Y. Grohens, *Eur. Phys. J. E* **38**, 56 (2015).
- ⁷ J. K. Bal, T. Beuvier, A. B. Unni, E. A. Chavez Panduro, G. Vignaud, N. Delorme, M. S. Chebil, Y. Grohens, and A. Gibaud, *ACS Nano* **9**, 8184 (2015).