УДК 539.32+620.172.225

POSSIBLE CAUSES OF YOUNG MODULUS JUMP NEAR TO A SURFACE OF THE THIN POLYMER FILMS

M. A. Zhytkova[1], Z. Rymuza[2], S. A. Chizhik[1], L. Ocypa[2]

[1] *A.V. Luikov Heat and Mass Transfer Institute of National Academy of Sciences of Belarus, P. Brovki str., 15, Minsk, Belarus. E-mail: mzhytkova@gmail.com*
[2] *Warsaw University of Technology, Institute of Micromechanics and Photonics, ul. Sw. A. Boboli, 8, 02-525 Warsaw, Poland. E-mail: z.rymuza@mchtr.pw.edu.pl*

Young modulus of different polymer films has been measured that showed its high values in the beginning of the indentation near a surface and immediate unexpected incidence after some depth. Possible causes of this phenomenon connected with a glass transition temperature reduction and chain mobility are reviewed.

Introduction

Thin films on substrates are a matter of considerable study because of their practical usefulness. The increasing number of applications for polymer thin films has spurred a surge of activity aimed in increasing our understanding of the properties of these materials. There are numerous deposition techniques developed to enrich polymers properties and make a field of their application wider. The commonly used method to investigate material properties is indentation testing that can be applied for determination of elastic properties, such as Young modulus of the material. There were realized some experiments that showed high Young modulus of the films in the beginning of the indentation near a surface and immediate unexpected incidence after some depth. It is anomalous phenomenon, which might be explained in different ways. Polymers in a thin film configuration may have physical properties different from those of the bulk systems due to interfacial interactions and effects of molecular confinement. The nature of the glass transition is still imperfectly understood in bulk systems and even less is known about the effects of system size and surfaces on the transition.

Experimental section

We have investigated two samples of poly(methyl methacrylate) (PMMA) films with 100 nm thickness by force spectroscopy technique of an atomic-force microscopy NT-206 produced by Microtestmachines, ltd. We have used a cantilever with the spring constant of 6 N/m and indenter curvature radius of 63 nm by Micromash. An indentation has been arranged in three different points on the surface of each sample. To estimate elastic properties of the films Young modulus versus indentation depth curves have been drawn after data processing. Received curves are shown in fig.1. For the indentation depth of 2 nm for a first sample and of 7 nm for another high jump of the Young modulus of the films is seen, after that an immediate incidence to 0.13–0.4 GPa occurs. We can also mention that for the second sample with higher Young modulus near the surface a maximal indentation depth is almost two times less than for the first film.

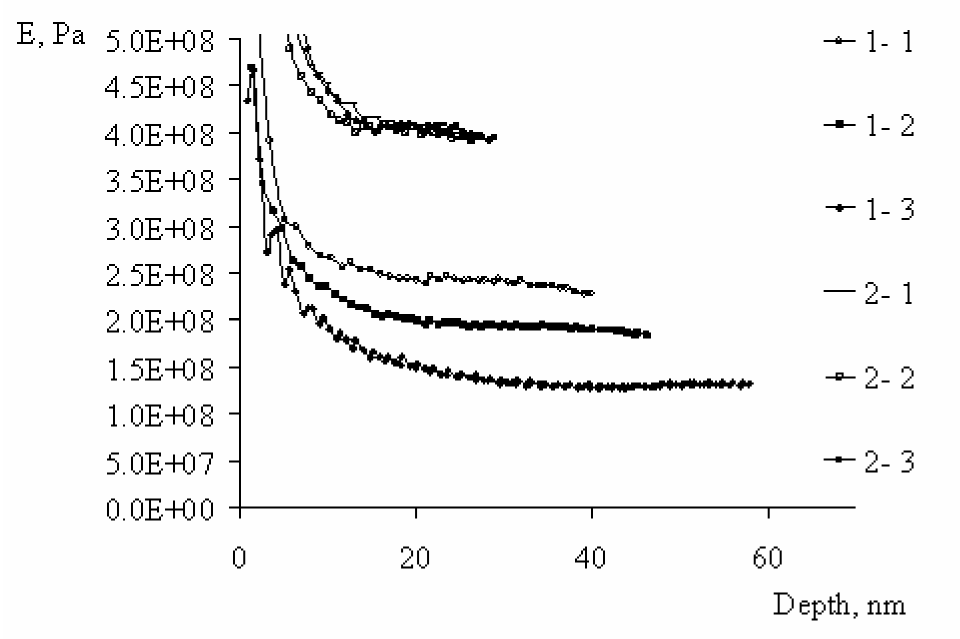

Fig. 1. Young modulus versus indentation depth curves: three points for indentation for the first sample 1 (1-1, 1-2, 1-3) and three points (2-1, 2-2, 2-3) for the second sample 2

Discussions

After the experiment some researches [1–8] about polymer thin films have been studied that explain some possible causes of that anomalistic Young modulus jump.

J.L. Keddie [1] measured *Tg* as a function of film thickness by detecting with ellipsometry the discontinuity in expansivity as the films are heated at a constant rate. It was found that the glass transition decreases in temperature as the thickness of the film is reduced. The results of one of these experiments are shown in fig. 2.

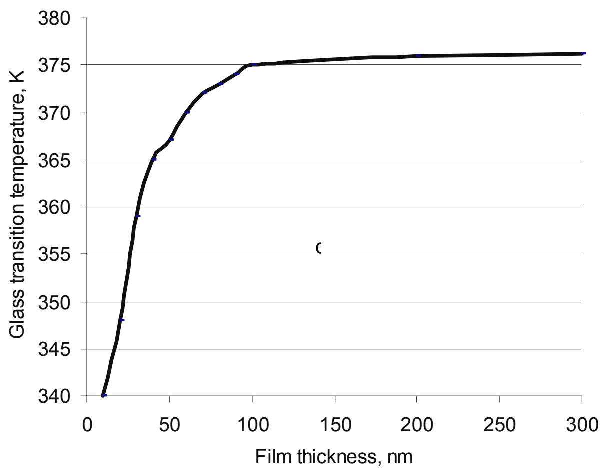

Fig. 2. General viewof the glass transition temperature Tg as a function of film thickness for polystyrene

These results allow to think that at relatively low temperatures near-surface layer of the very thin polymer films can vitrify and there will be like “an ice crust” on the surface. When the indenter meets the surface and this layer it is needed more stress to hole the crust. After it is holed the indenter does not have any difficulty and Young modulus comes to the normal for that polymer film values.

We should also mention one other possible cause of a thickness-dependent *Tg* in thin films supported by a substrate. The development of a disjoining pressure across the thin film as a result of van der Waals interactions could lead to a change in density and thus in Tg, but this mechanism was ruled out by showing that the predicted change in Tg is of a smaller order of magnitude than the changes Keddie et al. observed.

A simple and reliable curves has been suggested by V.N. Bliznyuk [7]. The values of the surface glass transition for the technique for measuring the surface glass transition based on analysis of SFM force-distance samples with molecular weight *Mn* more than 30 000 have been found to be the same as the corresponding bulk values. The molecular mass dependence of *Tg* (fig. 3) correlates with the structural and dynamical parameters of polymer chains: the presence of the virtual network of labile entanglements. Molecular entanglement rather than chain-end segregation effects are responsible for the depression of *Tg* at the surface.

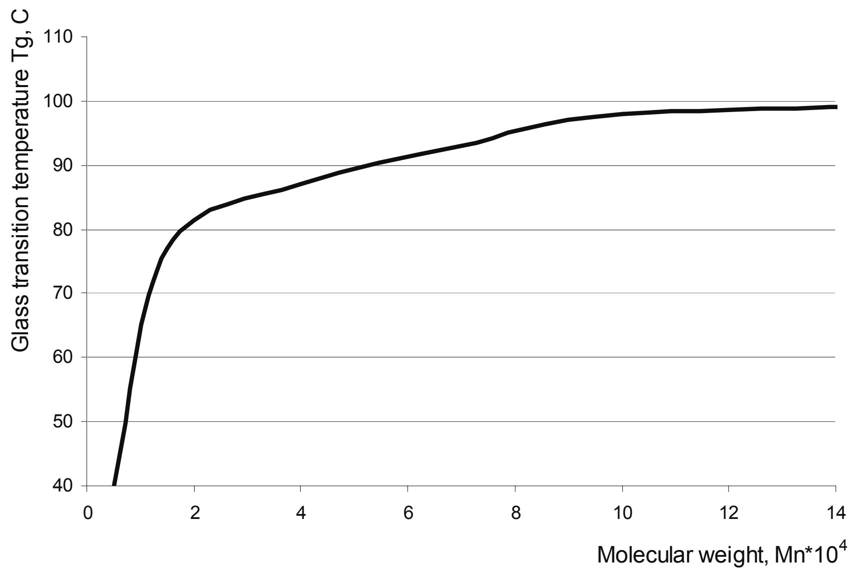

Fig. 3. Surface glass transition temperatures as determined like SFM experiments versus *Mn*

It needs to be said that during fracture of polymers below the bulk *Tg* there is substantial evidence for chain disentanglement in crazy fibrils and active zones [1], which might separately have any other way of a behavior and have not such high characteristics of elasticity as in the cooperated system. Furthermore, if the picture of a near-surface region with mobility greater than in the bulk is correct, this will be implications for mechanisms of sintering of polymer colloids that will prevent simplicity of indentation at first time and show high Young modulus.

Conclusions

We have observed near-surface jump of Young modulus of thin polymer films and discussed possible causes of this phenomenon. The main cause of this fact can be the reduction of the glass transition temperature with the decreasing film thickness that leads to a vitrified layer formation on the surface of the film that needs additional stress from the indenter. From another point of view, molecule mobility increases while the film thickness reduces that makes chain entanglement be the barrier on indenter's way.

The work was partly financed in the frame of the State Complex Programme for Scientific Research "Mechanics", the Project 2.19, and the Project F08R-212 of Belarusian Republican Foundation for Fundamental Research.

References

1. Keddie J.L., Jones R.A.L., Cory R.A. // Europhysics Letters. 1994. Vol. 27. Pp. 59–64.
2. Keddie J.L., Jones R.A.L., Cory R.A. // Faraday Discussion. 1994. Vol. 98. Pp. 219–230.
3. Forrest J.A,. Dalnoki-Veress K., Stevens J.R., Dutcher J.R. // Physical Review Letters. 1996. Vol. 77. Pp. 2002–2005.
4. Forrest J.A., Svanberg C., Revesz K., Rodahl M.,.Torell M.L., Kasemo B.// Physical Review E. 1998. Vol. 58. Pp. 1226–1229.
5. Frank B., Gast A.P., Russell T.P., Brown H.R., Hawker C. // Macromolecules. 1996. Vol. 29. Pp. 6531–6534.
6. Fryer D.S., Nealey P.F., de Pablo J.J. // Macromolecules. 2000. Vol. 33. Pp.64396447.
7. Bliznyuk V.N., Assender H.E. Briggs G.A.D. // Macromolecules. 2002. Vol. 35. Pp.6613–6622.
8. Pratt F.L., Lancaster T., Brooks M.L., Blundell S.J., Prokscha T., Morenzoni E., Suter A., Luetkens H., Khasanov R., Shinotsuka K., Assender H.E. // M.Physical Review B. 2005. Vol. 72. Pp. 121401-1–121401-4(R).