

Dynamic microprobing of viscoelastic polymer properties

Vladimir V Tsukruk,^{1*} Valery V Gorbunov,² Zheng Huang¹ and Sergey A Chizhik²

¹College of Engineering and Applied Sciences, Western Michigan University, Kalamazoo, MI 49008-5062, USA

²Metal–Polymer Institute, National Academy of Science, Gomel, 246550, Belarus

Abstract: Scanning force microscopy (SFM) was used to probe the micromechanical properties of polyisoprene rubbers, polyurethanes, polystyrene and polyvinylchloride. Applicability of the SFM cantilevers for microprobing is presented as a convenient method for materials selection. The Hertzian model of elastic contacts was used to obtain Young's modulus at contact frequencies range 0.05–367 Hz. The absolute values of the elastic modulus were correlated with the known properties of bulk materials, with no frequency dependence detected for glassy polyvinylchloride and polystyrene in air. The time dependence of the Young's modulus of rubber and polyurethanes followed the Williams–Landel–Ferry relationship, with parameters known for bulk materials. For PVC in water, a significant reduction of the elastic modulus and strong time-dependency were recorded. This behaviour can be related to the lower local glass transition temperature because of a plastification effect of solvent molecules on the uppermost polymer layer.

© 2000 Society of Chemical Industry

Keywords: scanning probe microscopy; atomic force microscopy; micromechanics of polymers; viscoelastic behaviour; polymer surfaces

INTRODUCTION

Microprobing mechanical properties of the surface layers of polymeric materials with submicronmetre resolution became a reality after the introduction of the scanning force microscopy (SFM) technique.^{1,2} Several recent publications have demonstrated that stable and quantitative results could be obtained for a variety of polymers.^{3–6} In the present communication, we report the results of probing dynamic micromechanical properties at indentation depths of 2–200 nm for viscoelastic polymeric materials with absolute values of Young's modulus E ranging from 2 MPa to 4 GPa: polyisoprene rubbers (NR), polyurethanes (PUs), polystyrene (PS), and polyvinylchloride (PVC).

EXPERIMENTAL

The samples for investigation were selected to represent a variety of polymeric materials with a wide range of viscoelastic properties. Polyisoprene rubber, M_w of 800 000 (Aldrich) had a glass transition temperature T_g of -73°C and an E value of 1.9 MPa. Polyester-based S60D53N and S69D53N Elastollan polyurethanes (BASF) and Dyreflex PT92004 (Bayer) had their T_g in the range -30 to -40°C and E in the

range 20–30 MPa and 18 MPa respectively. Polyvinylchloride was Selectophore from Fluka with T_g 78°C and E of about 0.8 GPa. Polystyrene with an M_w of 250 000, T_g of 100°C and E of 1.2 GPa was obtained from Janssen Chimica.

Smooth homogeneous polymer films of 0.5–5 μm thickness were prepared by the spin-coating technique from dilute solutions. Glass transition temperatures were obtained from differential scanning calorimetry with a heating rate of 10–20 degrees per minute. Young's moduli for cast polymeric films were measured by tensile testing with an Instron 4301 instrument at elongation speeds varying from 2 to 300 mm min^{-1} . A Dimension 3000 (Digital Instruments, Inc) was used to characterize surfaces of spin-coated polymer films according to a well-established procedure.^{7,8} To evaluate the micromechanical properties, we analysed 10–20 force–distance curves measured at 3–6 randomly selected locations, using an approach–retract frequency in the range 0.05–367 Hz.

We used a set of silicon and silicon nitride V-shaped cantilevers with nominal spring constants k_n from 0.06 to 47 N m^{-1} ; stiffer cantilevers were applied to harder materials. Actual values of spring constants were determined by the fundamental resonant frequency calibration proposed earlier,⁹ and cross-checked by

* Correspondence to: Vladimir V Tsukruk, College of Engineering and Applied Sciences, Western Michigan University, Kalamazoo, MI 49008-5062, USA

E-mail: vladimir@wmich.edu

Contract/grant sponsor: National Science Foundation, USA; contract/grant number: CMS-94-09431; contract/grant number: CMS-96-10408

Contract/grant sponsor: Becton Dickinson Corp

(Received 11 February 1999; accepted 11 May 1999)

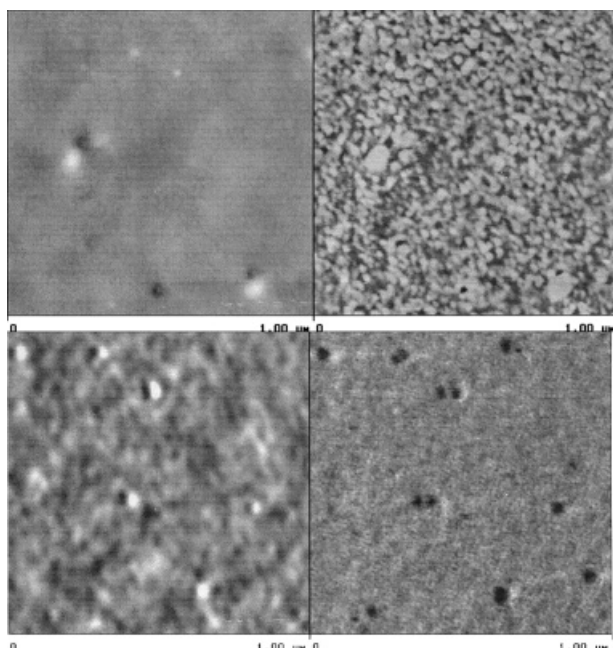


Figure 1. Topography (left) and phase (right) images of spin-coated films of Dyreflex polyurethane (top, vertical scale for topography is 20 nm) and PVC (bottom, vertical scale for topography is 2 nm).

both the cantilever-against-cantilever technique and the added mass technique. Tip radii were measured using mixed gold nanoparticles and varied in the range 20–60 nm, from tip to tip. The elimination of the strong capillary forces was achieved by scanning in fluid (nanopure water and/or absolute alcohol).

RESULTS AND DISCUSSION

The surface morphology of all samples was observed in tapping mode in air (Fig 1). On the micrometre scale, the surface of all spin-coated films is homogeneous for PS, PVC and rubber samples. These films possess microroughness (calculated within a $1 \mu\text{m} \times 1 \mu\text{m}$ area) in the range 0.2–0.8 nm. A light grainy texture caused by microdomain structure is observed for all PU samples (see an example in Fig 1).^{3,4} The PU samples show higher microroughness, which can reach 3–4 nm. Phase imaging of polymeric materials shows relatively even surface distribution of phase shift, indicating homogeneous distribution of chemical composition and viscoelastic properties (Fig 1; note some local spikes caused by the presence of submicrometre foreign inclusions and holes).

SFM cantilevers are considered as a probing tool for a wide range of polymers.^{10,11} Here, we define the limits of detection of surface deformation which were determined by analysing the ratio of materials elasticity and spring constant of cantilevers. If the cantilever is too stiff the vertical deflection of the SFM cantilever, z_{defb} , is very small compared to z_{pos} , the vertical displacement of the piezoelement. In this case, the ratio T , of indentation depth $h = z_{\text{pos}} - z_{\text{defb}}$, to total

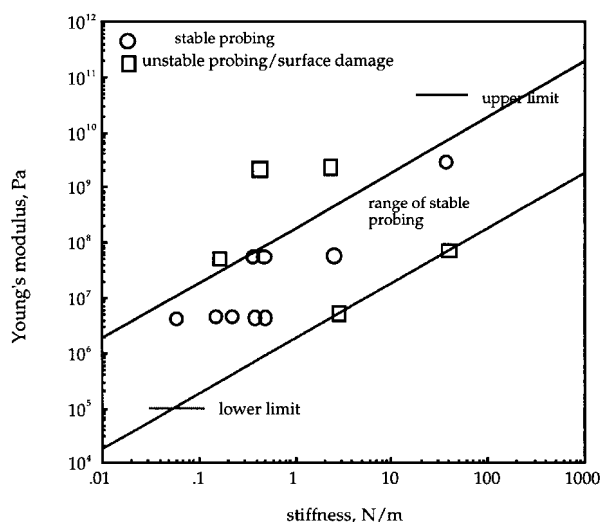


Figure 2. Range of applicability of cantilevers with different stiffness with limits $h/z_{\text{defb}}=0.1$ (upper limit) and $h/z_{\text{defb}}=10$ (lower limit) and tested cantilevers for various materials (marks).

displacement reaches an upper measurable limit:

$$T = h/z_{\text{pos}} \rightarrow 1 \tag{1}$$

However, if the material is much harder than the cantilever stiffness, then $z_{\text{pos}} \approx z_{\text{defb}}$, which results in a lower limit of observation

$$T = h/z_{\text{pos}} \rightarrow 0 \tag{2}$$

Apparently, unambiguous measurements of materials properties are possible only far from these limits. For further estimations, we assume that the ratio of indentation depth and cantilever deflection should not lie outside the ratios 1:10 and 10:1. This condition, in our opinion, takes into account a usual level of noise and non-linearities of a commercial mechanical system, and provides an acceptable signal level which can be separated from background.

Using these deflection/indentation conditions, we estimated the range of ratios between the elastic modulus of materials and cantilever spring constants, which satisfies the measurable limits discussed above (Fig 2). For these estimations we used the Hertzian model of elastic contact and a two-spring model as discussed before.¹² As is clear from the plot presented, choosing the optimal spring constant within the range $0.01\text{--}100 \text{ N m}^{-1}$ should allow measurements of elastic moduli from as low as tens of kPa to as high as tens of GPa. This range of elastic moduli spans the vast majority of polymeric materials ranging from gels to hard plastics.¹³ However, using a cantilever with a given stiffness for surface mapping limits the range of elastic modulus variation by not more than 2–3 orders of magnitude. To test the validity of the proposed method, we used a variety of commercially available cantilevers to probe elastic properties and estimate the reliability of the limits proposed. As can be seen from the data points for the various cantilevers tested here,

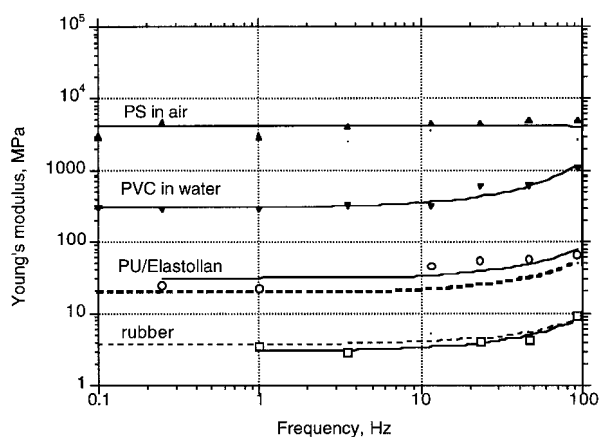


Figure 3. Time dependence of elastic modulus for PS, PVC, natural rubber and Elastollan PU. Dashed curves represent time-dependent elastic moduli calculated from the WLF equation for natural rubber and polyurethane by using known parameters for bulk materials and for PVC assuming lower glass transition temperature.

we obtained unstable results or surface damage beyond the defined limits (Fig 2).

The equations for the calculation of Young's modulus from cantilever deflection data can be derived by using a two-spring linear model of interacting cantilever spring and elastic surface.¹² This approach gave consistent values of elastic moduli for indentation depth up to 100–200 nm with lateral resolution better than 10–100 nm for most polymeric materials. Here, we discuss the results on the calculation of Young's moduli of polymer surface layers, as probed by SFM at different contact frequencies.

As was observed, both glassy polymers (PVC and PS) in air showed no time dependence of elastic modulus within the frequency range 0.05–100 Hz (Fig 3). elastic modulus is 4.0 ± 1.0 GPa for PS and 1.0 ± 0.2 GPa for PVC. However, for PVC in water, Young's modulus decreased significantly. Strong frequency dependence was observed for PVC in water and alcohol: Young's modulus increased from 200 MPa at low frequencies to 1 GPa for high frequencies. A similar increase of elastic modulus was observed for elastic rubber and PU materials (Fig 3). In this case, Young's modulus rises from 2.9 MPa for rubber and 30 MPa for Elastollan PU to 9 MPa and 70 MPa, respectively.

This time-dependent behaviour is well known for elastomers and can be described within the Williams–Landel–Ferry (WLF) approach and by using viscoelastic models.^{13,14} Indeed, the Maxwell model of viscoelastic behaviour predicts exponential damping of elastic modulus with increasing time, that is close to the behaviour observed for rubber and PUs. We used WLF equation with generic parameters commonly used for bulk rubbers and PUs¹³ to generate the dynamic behaviour expected for these materials (Fig 3). As can be concluded from direct comparison of the calculated and measured data, the WLF formalism describes the viscoelastic behaviour of rubber and

polyurethane surface layers adequately with dynamic parameters close to the bulk values.

A significant reduction of PVC modulus in water and strong time dependence indicate that the micro-mechanical properties of PVC surface layer in these solvents differ from the glassy bulk properties. These changes can be related to the partial penetration of solvent molecules in the very uppermost surface layer (30–40 nm) (plastification effect).¹³ As a result of this, the surface layer enriched with low-molar mass molecules provides higher mobility for macromolecules and the local T_g is shifted downwards. By using the WLF equation, we calculated this 'apparent' glass transition temperature for the uppermost surface layer. The observed time dependence gives a T_g value of 35°C for the PVC surface layer in water compared to 78°C for the bulk material. This shift can be expected for PVC containing about 20% of low molar mass plastisizer.¹³

CONCLUSIONS

In conclusion, for rubber and polyurethanes we observed a surface behaviour which follows the Williams–Landel–Ferry relationship with the parameters known for bulk materials. No frequency dependence was observed for glassy polymers (PS and PVC) in air. For PVC in water, a strong time-dependency of Young's modulus was recorded. This behaviour was related to the downshift of the local glass transition temperature, which could be caused by a plastification effect of solvent molecules on the uppermost polymer layer.

ACKNOWLEDGEMENTS

This work was supported by the Surface Engineering and Tribology Program, the National Science Foundation Grants CMS-94-09431 and CMS-96-10408, and Becton Dickinson Corp. The donation of polyurethane materials by BASF and Bayer is greatly appreciated.

REFERENCES

- 1 Binnig G, Quate CF and Gerber Ch, *Phys Rev Lett* **12**:930 (1986).
- 2 Sarid D, *Scanning Force Microscopy*, Oxford University Press, New York (1991).
- 3 Hues SM, Colton RJ, Meyer E and Guntherodt H-J, *MRS Bull* **18**(1):41 (1993).
- 4 Ratner B and Tsukruk VV, *Scanning Probe Microscopy of Polymers*, ACS Symposium Series 694, ACS, Washington DC (1998). ACS
- 5 Bhushan B, *Micro/Nanotribology and its Applications*, NATO ASI Series, Kluwer Dordrecht (1997).
- 6 Tsukruk VV Wahl K, *Microstructure and Microtribology of Polymer Surfaces*, ACS Symposium Series 741, ACS, Washington DC, (1999).
- 7 Tsukruk VV, *Rubber Chem Technol* **70**(3):430 (1998).
- 8 Bliznyuk VN, Hazel JH, Wu J and Tsukruk VV, in *Scanning Probe Microscopy in Polymers*, Ed by Ratner B and Tsukruk VV, ACS Symposium Series 694, ACS, Washington DC. p 252, (1998).

- 9 Hazel J and Tsukruk VV, *J Tribology* **120**:814 (1998).
- 10 Vanlandingham MR, McKnight SH, Palmese GR, Ellings JR, Huang X, Bogetti TA, Eduljee RF and Gillespie JW, *J Adhesion* **64**:31 (1997).
- 11 Vanlandingham MR, McKnight SH, Palmese GR, Eduljee RF, Gillespie JW and McCulough RJ, *J Mater Sci Lett* **16**:117 (1997).
- 12 Chizhik SA, Huang Z, Gorbunov VV, Myshkin NK and Tsukruk VV, *Langmuir* **14**:2606 (1998).
- 13 Aklonis JJ and MacKnight WJ, *Introduction to Polymer Viscoelasticity*, John Wiley, New York (1983).
- 14 Brandrup J and Immergut EH, *Polymer Handbook*, John Wiley, New York (1975).