CHAPTER 17

MECHANICAL PROPERTIES OF THIN POLYMER FILMS WITHIN CONTACTS

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This chapter addresses the problem of the mechanical properties of thin polymer films geometrically confined within contacts between elastic substrates. Analytical contact mechanics solutions for coated substrates are used to derive, within the limits of confined contacts situations, an approximate oedometric solution for the indentation of a thin film lying on a more rigid substrate. From a discussion of this approximate model, it is shown that lateral contact methods are an interesting alternative to indentation experiments for the measurement of the viscoelastic properties of polymer films in their glass transition range or rubbery state. As an example, the hydrostatic pressure dependence of the viscoelastic properties of confined polymer films is analyzed in the light of lateral contact stiffness measurements. The effects of hydrostatic pressure on the onset of plastic flow within confined polymer coatings are also discussed.

1. Introduction

Thin polymer films are widely used in many tribological applications where their mechanical properties are of primary importance. Within this context, contact experiments such as nanoindentation have emerged as a promising route for the measurement of the viscoelastic and plastic properties of thin polymer films. However, contacts on coated substrates are often characterized by a high level of geometrical confinement. Such a confinement results in very specific mechanical conditions which are characterized by high strain rates and/or elevated hydrostatic pressures within the coating. Polymers being very sensitive to these parameters, the mechanical response of confined coatings is thus likely to be very different from that of bulk polymer substrates. However, the implications of confinement on the measurement of the mechanical properties of thin films remain largely to establish. Such an issue relies on the development of appropriate coated contact models which can provide insights into the deformation modes of confined films. In the context of indentation, the analysis of experiments usually relies on contact mechanics models (such as the popular Oliver and Pharr model [1]) which were initially developed for isotropic and homogeneous solids. In the case of layered solids, these approaches are no longer valid when the deformation of the substrate comes into play, i.e. when the contact radius is of the order of about one tenth of the film thickness. Accordingly, indentation models are often modified by introducing the concept of an equivalent modulus which incorporates the depth dependent contributions of the film and the substrate. In order to extract the film modulus from this measured composite modulus, various empirical and semi-empirical models have been proposed on the basis of experimental data and finite element simulations. Most of them express the composite modulus as a linear or non linear combination of the modulus of the substrate and of the film [2-6]. Alternatively, analytical approaches have also been developed by Gao *et al* [7] in order to derive approximate expressions for the contact compliance within the limits of moduli ratios not exceeding a factor of two. These approaches have been successfully applied to nanoindentation experiments where the ratio of the contact radius to the film thickness remains close to unity, i.e. for contact conditions which are characterized by a low geometrical confinement. However, when the indentation depth becomes of the order of magnitude of the film thickness, there is some indications that the above mentioned indentation models can provide erroneous [8] or unexpectedly high [9] values of the layer Young's modulus.

In this chapter, we show that within the limits of confined contact geometries, an approximate solution for the elastic indentation of coated substrates can be derived from analytical contact mechanics solutions. This approximate solution will serve as a basis to discuss the adequacy of indentation experiments to measure the viscoelastic properties of confined polymer films. When such measurements are to be done with polymer coatings in their glass transition range or in the rubbery state, i.e. close to incompressibility, it turns out that lateral contact situations offer an interesting alternative to normal indentation. As an example, it will be shown how lateral contact experiments can be used to determine the hydrostatic pressure dependence of the linear viscoelastic properties of confined polymer films in their glass transition range. The effects of hydrostatic pressure will subsequently be analyzed in the context of plastic contact deformations. The onset of plastic flow in confined films will especially be discussed in the light of the pressure dependence of the yield stress in polymers.

2. Contact Mechanics of Confined Polymer Coatings

2.1. Oedometric Approximation for the Normal Indentation of Confined Layers

As reviewed by Fretigny *et al* [10], theoretical contact mechanics solutions for layered substrates have long been derived by integral transforms methods. Starting from the basic equations of elasticity and writing the boundary conditions at the interface between the layers, analytical expressions for the Fourier or Hankel transforms of displacements and stresses can be obtained for a prescribed distribution of the surface stresses.

This approach is applied here to the system depicted in Figure 1, which consists of a coated elastic substrate in contact with a rigid sphere. E_i and ν_i denote the Young's modulus and the Poisson's ratio of the layer (i=1) and of the substrate (i=0). An expression for the Green function of this coated system has been initially derived by Burminster [11] and rediscovered later by others [12-14]. It relates the Hankel transforms of the normal displacement, $u_1(r)$, to that of the applied normal stress, $\sigma(r)$, at the surface of the elastic layer:

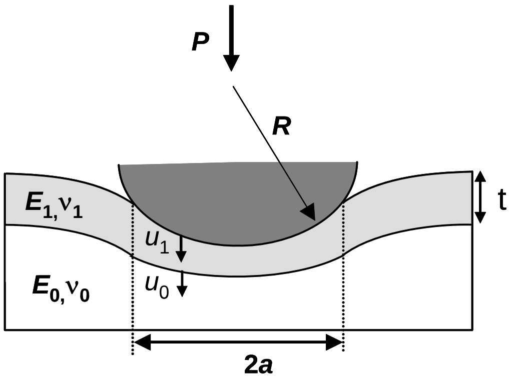

Fig. 1. Schematic description of the elastic indentation of a coated substrate by a rigid sphere. The layer is assumed to be perfectly bound to the substrate and the contact interface is frictionless. E_i and ν_i are the Young's modulus and the Poisson's ratio of the substrate (i=0) and the layer (i=1).

$$\bar{u}_1(\xi) = \frac{2}{E_1^*}\frac{X(\xi)}{\xi}\bar{\sigma}(\xi) \tag{1}$$

where E_1^* is the reduced modulus of the layer defined as $E_1/(1-\nu_1^2)$ and $X(\xi)$ is defined as:

$$X(\xi) = \frac{1 + 4b\xi t e^{-2\xi t} - abe^{-4\xi t}}{1 - \left(a + b + 4b(\xi t)^2\right)e^{-2\xi t} + abe^{-4\xi t}} \tag{2}$$

$$a = \frac{\alpha\gamma_0 - \gamma_1}{1 + \alpha\gamma_0}, \quad b = \frac{\alpha - 1}{\alpha + \gamma_1}, \quad \alpha = \frac{G_1}{G_0},$$

$$\gamma_1 = 3 - 4\nu_1, \ \gamma_0 = 3 - 4\nu_0$$

where G_0 and G_1 denote the shear moduli of the substrate and the layer, respectively. In equation (1), the quantities in the form of $\bar{q}(\xi)$ correspond to the 0th-order Hankel transform of the function $q(r)$ defined as:

$$\bar{q}(\xi) = \int_0^\infty dr r J_0(\xi r) q(r) \tag{3}$$

with $J_0(x)$ the 0th-order Bessel function of the first kind.

In a recent paper, Perriot and Barthel [15] have developed a semi-analytical methodology which allows the inversion of this Green tensor in the real space. Using, this approach, an exact solution is provided to the problem of the determination of the penetration and the contact load. It was also established by Fretigny and Chateaminois [10] that this theoretical model can also be extended to the calculation of the stress and displacement field within the layered substrate. It will be shown below that a simple approximation for the indentation response of a layered substrate can be derived, within the limits of confined contact geometries, from this exact contact mechanics solution.

In the above expressions, the Hankel transform of the fields are equivalent to their two-dimensional Fourier transforms, as they are radially symmetric. Then, as the normal stress is zero out of the contact area, it is expected that its Hankel transform varies at the scale of $1/a$. On another hand, we can deduce from its expression that $X(\xi)$ varies at the scale of $1/t$. Thus, in the case of confined contacts, i.e. $t \ll a$, it is presumably sufficient to consider a first order expansion of $X(\xi)$ in order to invert equation (1). Moreover, assuming that the layer modulus is much lower than the substrate one, the expansion can be written:

$$X(\xi) \approx \frac{2}{E_0^*} + \frac{1}{\tilde{E}_1}\xi t \qquad (4)$$

where the effective modulus, $\tilde{E}_1$, can be expressed in the following form:

$$\tilde{E}_1 = E_1 \frac{(1-\nu_1)}{[(1-2\nu_1)(1+\nu_1)]} \qquad E_1 \ll E_0 \qquad (5)$$

It can easily be recognized that $\tilde{E}_1$ is in fact the so-called oedometric or longitudinal bulk modulus of the layer, which corresponds to the elastic response of the constrained material under compression or extension, deformation in the lateral dimension being prevented [16, 17]. This finding is physically consistent with the expected deformation mode of a layer confined within a contact. Taking into account equation (4), it can be shown that equation (1) reduces to the following expression in the real space[18]:

$$u_1 - u_0 = \frac{t}{\widetilde{E}_1}\sigma \tag{6}$$

where u_0 denotes the vertical displacement of the interface. This expression shows that, at each location within the confined contact, the compression of the layer is proportional to the local value of the applied normal stress.

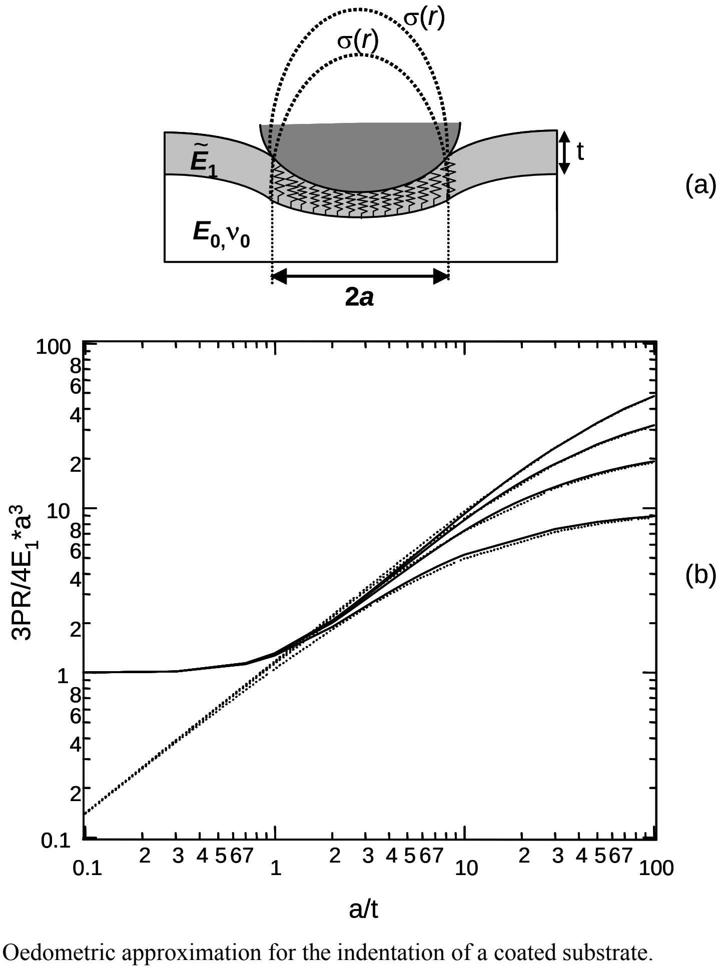

Fig. 2 Oedometric approximation for the indentation of a coated substrate.
(*a*) Approximate description of the indentation behaviour of a confined film lying on a more rigid substrate. $\widetilde{E}_1$ is the oedometric modulus of the layer.
(*b*) Non dimensional indentation load, $3PR/4E_1^*a^3$, as a function of the ratio of the contact radius, a, to the layer thickness, t. These curves were calculated for increasing values of the substrate to coating reduced moduli ratio. From bottom to top $E_0^*/E_1^* = 10$; $E_0^*/E_1^* = 25$; $E_0^*/E_1^* = 50$; $E_0^*/E_1^* = 100$; $E_0^*/E_1^* = 200$. The dotted lines correspond to the oedometric approximation schematized in (a), the continuous lines to the exact contact mechanics solution derived by Perriot and Barthel [15] for coated contacts. ($\nu_0 = 0.2$; $\nu_1 = 0.4$). From reference [18], with permissions.

Accordingly, it comes out that the indentation behaviour of the confined contact can be separated into two components (Figure 2a). The first one corresponds to the œdometric compression of the layer, which acts as a “mattress” of individual springs, each of them having the same compliance $t/\widetilde{E}_1$. It can be noted that this picture of the compressive response of the coating is very similar to that used by Johnson [19] in the so-called elastic foundation model for the contact between a sphere and a layer lying on a rigid substrate. Equation (6) can thus be viewed as an extension of this approach to the case of a deformable substrate, where the oedometric nature of the coating’s modulus is fully accounted for. The second component of the contact response corresponds to the elastic deformation of the substrate under the action of the contact stress applied over a contact area of radius, a.

An indication of the validity of this approximate description of confined contact is shown in Figure 2b where the normalized indentation load is represented as a function of the ratio, a/t, which describes the extent of the geometrical confinement of the contact. In addition to the curves corresponding to the above detailed oedometric approximation, calculations using a theoretical exact contact model derived by Perriot and Barthel [15] are also represented in the figure. It can be seen that when a/t is greater than about ten, the oedometric approximation allows for a very accurate description of the indentation behaviour. On the other hand, a systematic departure from the exact contact mechanics solution is systematically observed for low confinements. Such an insufficiency of the oedometric description in the low confinement regime is expected as the hypothesis of a non expansion of the normal contact stress outside the contact area is obviously no longer valid when the layer thickness is of the order of the contact radius.

Experimental elastic indentation data using glassy polymer films on glass substrates ($E_0^*/E_1^* \approx 50$, $\nu_1 \approx 0.4$) further support the validity of the oedometric description of confined contacts [18]. For such systems, it comes out that the application of the oedometric model to the data yield a value of the oedometric modulus which is consistent with that determined independently from compression testing of bulk specimens made from the same polymer.

Some comments are now in order regarding the indentation behaviour of confined polymer films in their glass transition range or in the rubbery state. In such a situation, polymers become close to incompressibility (i.e. $\nu_1 \rightarrow 0.5$) which corresponds to a sharp increase in their œdometric modulus (equation (5)). Since the compression of the film becomes strongly hampered, increased shear deformations are expected to come into play within the coating during the indentation process. Such deviations from a purely œdometric response of the confined layer are clearly evidenced by theoretical calculations of the $P(a)$ indentation curves. In Figure 3**,** it is shown that, when applied to nearly incompressible coatings, the œdometric approximation systematically overestimates the indentation loads as compared to exact contact mechanics calculations. This difference may be attributed to the fact that the exact model takes into account shear deformation within the layer,

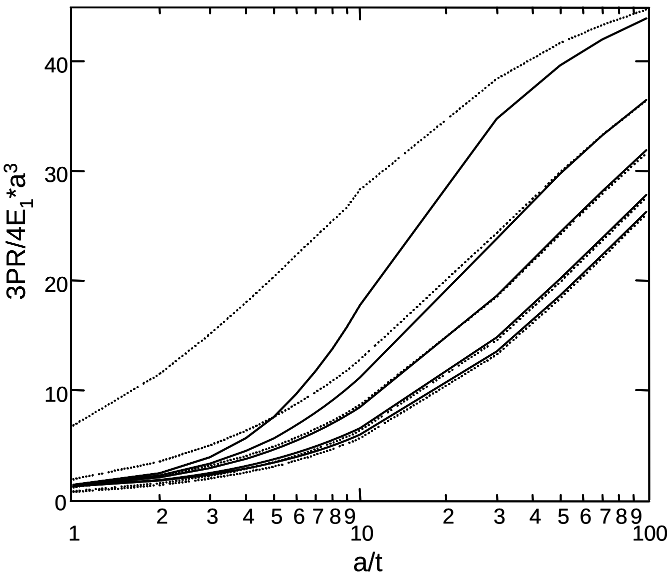

Fig. 3. Non dimensional indentation load, $3PR/4E_1^*a^3$, as a function of the ratio of the contact radius, a, to the layer thickness, t. These curves were obtained for increasing values of the Poisson's ratio of the coating. From bottom to top: ν_1=0.2; ν_1=0.3; ν_1=0.4; ν_1=0.45; ν_1=0.49. The dotted lines correspond to the oedometric approximation, the continuous lines to the exact contact mechanics solution derived by Perriot and Barthel [15] for coated contacts. (ν_0=0.2, E_0^*/E_1^* = 50). From reference [18], with permissions.

which in turn results in a decreased coating stiffness as compared to a purely œdometric response.

In addition, it is worth noting that the compressibility of the polymer coating also strongly affects the partitioning of the vertical displacement between the layer and the substrate. In the incompressible regime, the compression of the coating is penalized while the shear deformation of the layer is hampered by the confinement. In such a situation, the elastic deformation of the substrate should therefore predominate. An illustration of these effects is provided in Figure 4 where the vertical displacements of the surface and the film/substrate interface were calculated as a function of the Poisson's ratio of the layer and the confinement using an exact solution to the contact problem [20].

At low penetration ($a/t = 1$) the deformation of the substrate is limited and the response of the compressible and incompressible systems are close. As the contact radii are increased, the substrate starts to deform while the coating is increasingly confined. In this regime, the partitioning of the displacements between the substrate and the coating is strongly dependent on the compressibility of the layer. For an incompressible layer and $a/t = 8$, the surface displacement is almost completely due to substrate deformation; yet a roughly equal contribution from layer and substrate is calculated for a compressible material under the same condition of confinement.

Some practical conclusions may be drawn from these observations regarding the suitability of normal indentation tests to measure elastic properties of thin polymer films in their glass transition or rubbery domains. For common blunt indenters geometries such as Berkovitch tips, high levels of confinement are achieved within thin films even at low indentation depths. As a consequence, most of the measured contact stiffness is provided by substrate deformation and relative errors associated with the determination of the film response will therefore be enhanced. More importantly, Figure 3 shows that the indentation response becomes increasingly sensitive to small fluctuations in the Poisson's ratio close to incompressibility. Similar conclusions were also drawn from finite elements simulations of the flat punch indentation of thin films on rigid substrate [21]. In this study, the contact stiffness was found to depend strongly to the value of Poisson's ratio up to the 4st decimal close to 0.5.

This sensitivity to the Poisson's ratio close to incompressibility therefore strongly questions the accuracy of Young's modulus measurements of thin films using normal indentation, as ν_1 is generally not known with the required precisions. As it will be detailed below, lateral contact methods do not show such a dependence to the Poisson's ratio of the layer. They are therefore much more suitable for the mechanical characterization of polymer coatings close to incompressibility which encompasses many systems such as gels, soft

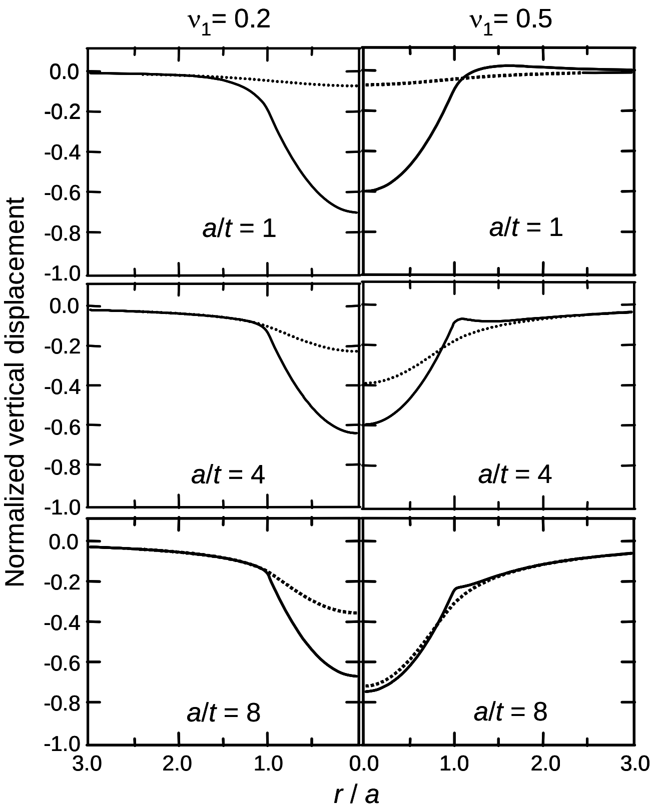

Fig. 4. Computed normal displacement of the surface (plain) and interface (dashed) for the contact of a sphere with a coated substrate. Radii are normalized with respect to contact radius, a, displacements with respect to a^2/R. The coating Poisson ratio is $\nu_1 = 0.2$ on the left, 0.5 on the right. ($\nu_0 = 0.2$, $E_0^*/E_1^* = 50$). From reference [20],with permissions.

adhesives and polymer films in their glass transition or rubbery zone.

2.2. *Lateral Contacts*

The above analysis of the indentation response of a confined coated substrate can readily be extended to a lateral contact loading. We will restrict ourselves to the case where the applied lateral displacement is low enough to prevent any significant micro-slip to occur at the contact interface. In such a situation, the contact response incorporates two components, namely the shear deformation of the film and the lateral contact response of the substrate. Of particular interest is the relationship between the lateral contact stiffness and the shear modulus of the film. As for normal contact configurations, it can be assumed that stresses within the layer do not expand out of the contact zone. The stress applied to the surface is therefore integrally transmitted to the substrate over a constant contact area. Within the limits of confined contact geometries, the layer and the substrate can be considered as two separate stiffnesses in series[22]. Assuming a pure shear response for the coating and neglecting edge effects, the stiffness, k_f, of the film disk enclosed within the contact is simply given by:

$$k_f = \pi G_1 \frac{a^2}{t} \tag{6}$$

where G_1 is the shear modulus of the film.
The second component involved in the lateral response corresponds to the contact deformation of the substrate. The associated stiffness, k_s, is given by the classical Mindlin's theory [23]:

$$k_s = 8G_0^* a \tag{7}$$

where G_0^* is the reduced shear modulus of the substrate defined by:

$$G_0^* = \frac{G_o}{2-\nu_o} \tag{8}$$

The film and the substrate behaving as stiffnesses in series, the overall contact stiffness, k_c, can thus be expressed as follows:

$$\frac{1}{k_c} = \frac{1}{k_f} + \frac{1}{k_s} \tag{9}$$

which can be rewritten as:

$$k_c = \frac{8G_0^* a}{1 + \frac{8}{\pi}\frac{G_0^*}{G_1}\frac{t}{a}} \tag{10}$$

This equation provides the basis to relate the measured contact stiffness, k_c, to the shear modulus, G_1, of the film. As mentioned above, the important point is that, as opposed to the normal indentation approximation which involves a $(1-2\nu_1)^{-1}$ factor, this lateral contact model behaves smoothly with respect to all parameters. Its application to the determination of the linear viscoelastic properties of confined polymer films through their glass transition zone is considered below.

3. Viscoelastic Properties of Confined Polymer Films in the Glass Transition Range

3.1. *Linearity of the Contact Lateral Response*

From an experimental point of view, the determination of the linear viscoelastic properties of polymer films by lateral contact methods involves the measurement of the contact stiffness under imposed cyclic relative displacements at various frequencies and temperatures. If large displacement amplitudes are considered, sliding friction takes place. In such a situation, the non linearities in the contact response make impossible the determination of the linear viscoelastic properties of the layer. However, when the displacement amplitude is reduced below the contact size, a Mindlin's type situation can be encountered where the contact can be divided into two regions: a central zone where no relative displacement of both surface occurs and an outer region where micro-slip takes place. If the lateral displacement amplitude is kept low enough, one can neglect the partial slip within the outer region and describe the cyclic lateral loading as the drag of the sample surface by the slider. Under such condition, the contact response becomes linear since it only involves the viscoelastic response of the film and the elastic deformation of the substrate. Accordingly, the shear viscoelastic modulus can be determined from the lateral contact stiffness using equation (10). In order to check the existence of such a linear regime, experiments can be carried out at increasing displacement amplitudes. An example is shown in figure 5 in the case of a glass substrate coated with an acrylate film about 20 µm in thickness in macroscopic contact with a glass sphere.

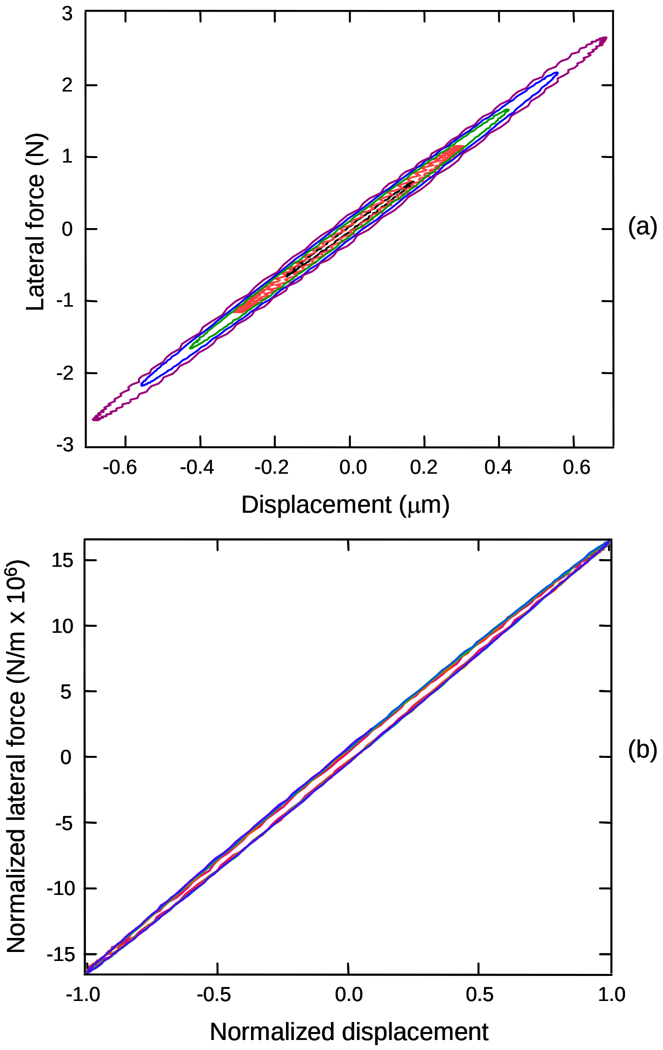

Fig. 5. Lissajou representation of the lateral force as a function of the applied relative displacement for a glassy acrylate film (33 µm in thickness) confined within a macroscopic contact between glass substrates (3.2 Hz, R.T.). (*a*) cycles obtained at increasing displacement amplitudes between 0.2 and 0.65 µm (*b*) same data as in (*a*) after normalization with respect to the amplitude of the applied displacement. The superimposition of the Lissajou cycles in this representation is a proof of the linearity of the contact lateral response.

When the Lissajou curves giving the lateral force as a function of the displacement are normalized with respect to the displacement amplitude, they become nearly superimposed. This demonstrates that, in the considered range of displacement amplitude, the contact response is linear.

3.2. *Pressure Dependance of the Linear Viscoelastic Modulus*

When considering confined films in their glass transition zone, it emerges that the applied contact pressure can induce major changes in the linear viscoelastic properties as compared to the bulk polymer at ambient pressure. In Figure 6, the storage modulus, *G*', and the loss tangent, tanδ, of confined films is represented as a function of temperature for increasing contact pressures. As expected, the glass transition of the films is associated with a drop in *G*' and a damping

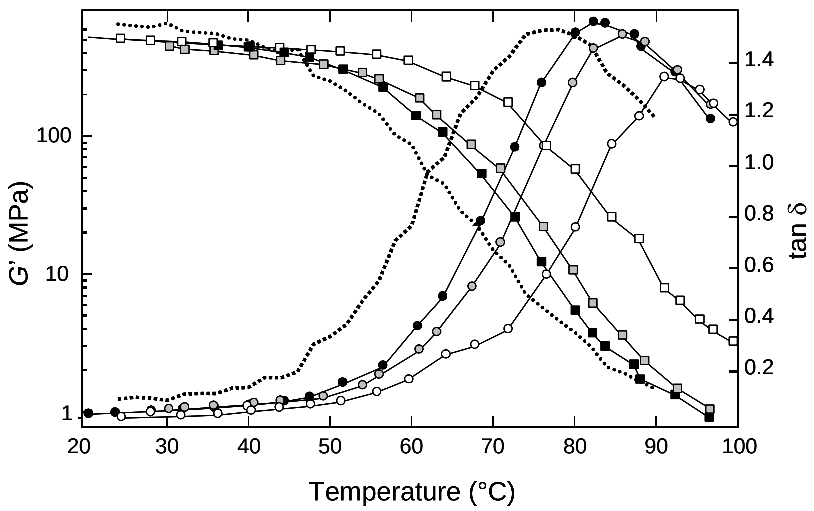

Fig. 6. Storage modulus, *G*', and tangent of the loss angle, tan δ, of confined polymer films determined from lateral contact stiffness measurements. Circles: tan δ, squares : G'. The tests have been carried out at increasing applied normal loads. Black symbols: P = 40 N; grey symbols : P = 100 N; open symbols : P = 240 N;. (frequency = 3.2 Hz, film thickness = 33 µm). The dotted lines correspond to the values of *G*' and tan δ measured by the same contact method using a bulk acrylate specimen, i.e. under unconfined conditions (from reference [24], with permissions).

peak. For an unconfined contact with a bulk specimen (dotted line in figure 6), the data are perfectly consistent with independent viscoelastic measurements using conventional Dynamic Mechanical Thermal Analysis (DMTA) [24]. On the other hand, a shift of the glass transition to high temperatures is clearly seen when increased contact pressures are applied to confined films. Such a shift can be attributed to hydrostatic pressure dependence of the glass transition of polymers. Within confined contacts, the hampered shear deformation results in the development of stresses of essentially hydrostatic nature when a normal contact loading is applied. As reviewed in references [25, 26], it is well known that the viscoelastic relaxation times of polymer glasses are strongly increased under static hydrostatic pressure. Qualitatively, this behaviour can be understood in terms of the dependence of the segmental mobility on the free volume since the free volume must decrease with increasing pressure just as it does with decreasing temperature. The occurrence of such effects within confined contacts is supported by the fact that the measured contact pressure dependence of the glass transition of the films (about 0.3 °C/MPa for acrylate coatings) is of the same order of magnitude than that measured using bulk polymers under hydrostatic pressure [18]. It can be noted in passing that hydrostatic pressure effects, although of more limited amplitude, have also been reported by Briscoe *et al.* [27] in the context of sliding friction of polymer films, close to their glass transition.

More generally, the temperature and pressure dependence of the linear viscoelastic properties of confined films in the glass transition zone can be described by means of a temperature-pressure superposition principle which is analogous to the well known time-temperature superposition principle. In Figure 7, the changes in the storage modulus as a function of the contact pressure are represented for various temperatures in the glass transition zone. When shifted along the pressure axis, these isotherms provide a master curve giving the changes in G' as a function of pressure for the considered reference temperature. As shown in the insert box, the shift factor, a_p, is roughly linearly related to temperature. It emerges from these results that a relatively moderate change in the contact pressure can result in very significant changes in the shear viscoelastic modulus of confined films.

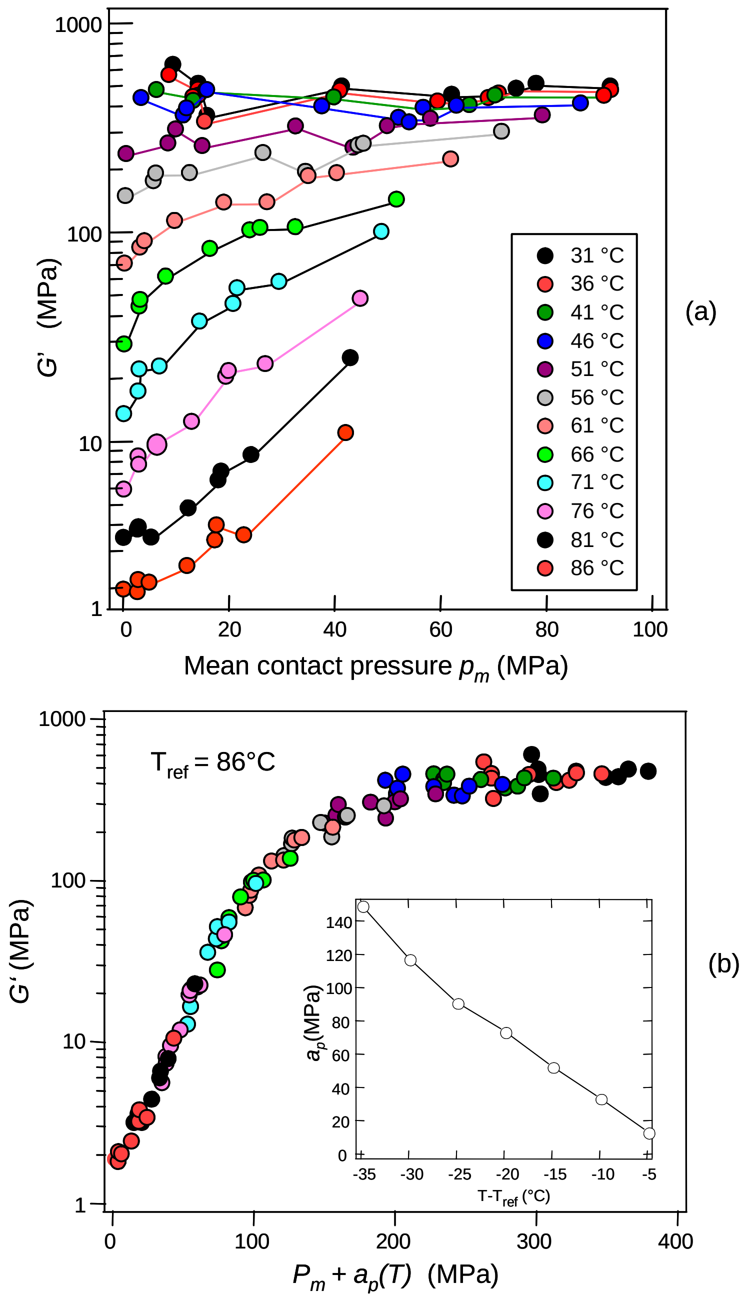

Fig. 7. Pressure-temperature superposition for confined glassy polymer films.
(*a*) Isotherms giving the storage modulus, *G*', as a function of the mean contact pressure at a frequency of 3.2 Hz.
(*b*) Master curve obtained by shifting the isotherms in (*a*) along the pressure axis. a_p is the shift factor. As shown in the insert box, it is roughly linearly related to the temperature with $da_p/dp_m \approx 44$ MPa/°C (the glass transition of the film at ambient pressure is 78°C at the considered frequency).

For the example in Figure 7, it is seen that the application of a contact pressure of 200 MPa is sufficient to induce the vitrification of an initially rubbery film, i.e. a change in the storage modulus of nearly three orders of magnitude.

4. Plastic Properties of Confined Polymer Films

Hydrostatic pressure is also known to affect the yield properties of bulk polymers. Early studies by Rabonwitz and co-workers [28] have revealed a substantial increase in the shear yield stress of glassy polymers such as PMMA up to an hydrostatic pressure of about 300 MPa above which brittle failure occurs. In the context of polymer tribology, this pressure dependence of the yield process has sometimes been invoked to analyse the sliding friction of thin polymer films [29-31]. From the similarities between the contact pressure dependence of the frictional stress and the hydrostatic dependence of polymer yield stress, it was argued that frictional dissipation within confined films results essentially from a plastic flow phenomenon. We will show here that hydrostatic pressure effects can also be involved during plastic indentation of polymer films and affect both the onset of plastic deformation and the yield flow.

4.1 *Plastic Imprints under Normal Indentation*

When a rigid sphere is pressed against a bulk polymer above the elastic limit, plastic flow is known to be associated with the formation of a permanent spherical imprint on the surface when the load is removed. When the same experiment is carried out on a thin polymer film lying on a more rigid elastic substrate, completely different imprints are surprisingly observed after unloading. Instead of a spherical capped plastic imprint, it is seen that plastic flow is concentrated at the periphery of the contact zone, while no substantial permanent deformation is detected at the centre of the contact (Figure 8). This behaviour of confined film can be attributed to the essentially hydrostatic nature of the stress distribution at the centre of the contact. Within this region, reduced shear stresses are effectively associated with high values of the hydrostatic pressure which is known to increase the yield limit of polymers.

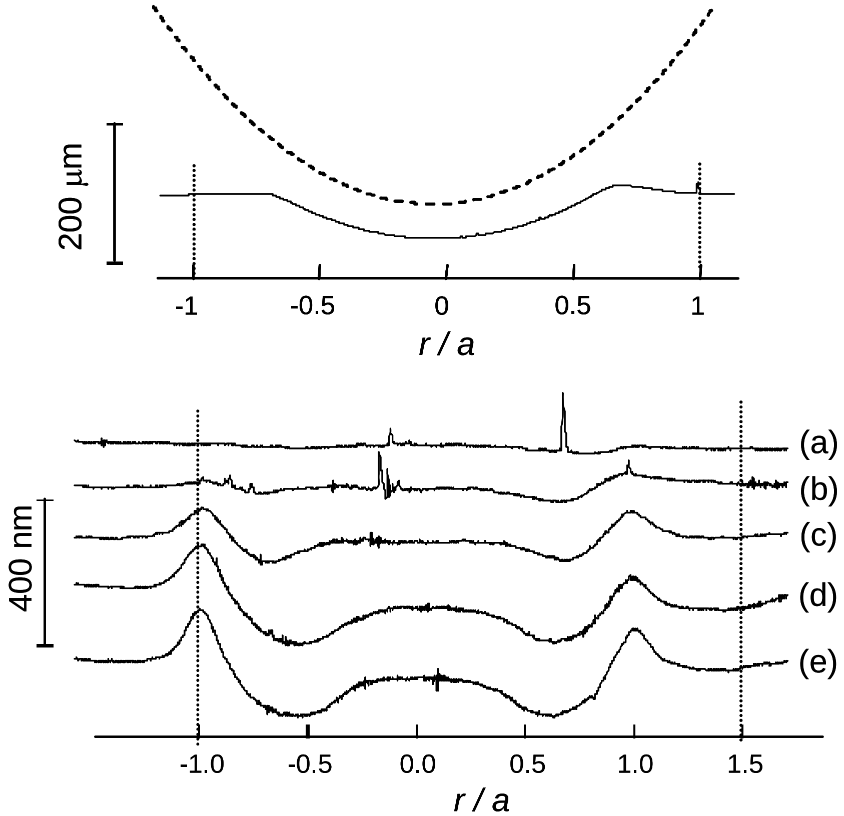

Fig. 8. Plastic imprints left on a polymer surface after sphere indentation.
Top: unconfined contact between a glass sphere and a glassy acrylate substrate.
Bottom: confined contacts between an acrylate film lying on an elastic glass substrate and a glass sphere. Experiments are carried out at different mean contact pressure $p_{m.}$ (*a*) p_m=56 MPa, a/t=6; (*b*) p_m=78 MPa, a/t=6.4; (*c*) p_m=131 MPa, a/t=8.6; (*d*) p_m=143 MPa, a/t=8.9 ; (*e*) p_m=171 MPa, a/t=9.6.

The occurrence of plastic flow is thus favoured at the periphery of the contact where the reduced confinement results in enhanced shear stresses and in a decreased yield limit as a result of the lowered hydrostatic pressure. This picture is supported by theoretical calculation of the stress

field induced within the coating. As a first approach, an elastic calculation can be coupled with some yield criterion in order to predict the location of the initial yield region within the coating.
Such a calculation can be carried out using an exact semi-analytical contact models for coated substrates [10], providing the results shown in Figure 9. The calculation of a simple von Mises stress from the elastic stress field (figure 9(I)) indicates that, for all the confinement levels

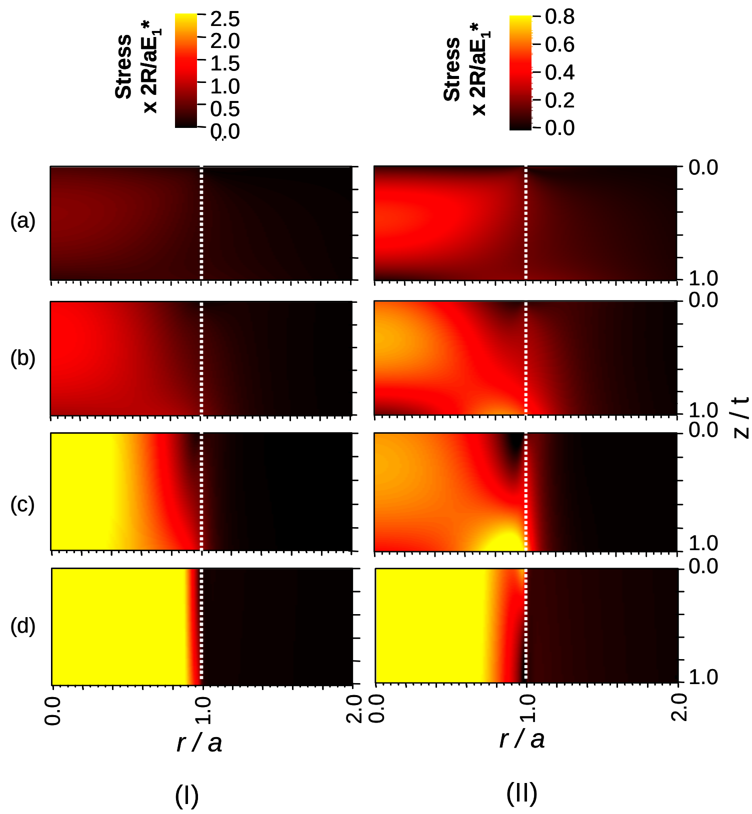

Fig. 9. Calculated non dimensional yield criteria within a coating in contact with a sphere as a function of the confinement level, *a*/*t*. (I) von Mises criterion (II) Pressure-dependent modified von Mises criterion, α=0.2. (a) *a*/*t* = 1; (b) *a*/*t* = 3; (c) *a*/*t* = 10; (d) *a*/*t* = 70. *a* is the contact radius, *t* is the thickness of the layer. For symmetry reasons, only one half of the contact zone is shown.

under consideration, the plastic deformation of the film should start at the center of the contact, as opposed to the experimental observation.

On the other hand, it emerges from the calculation of a modified, hydrostatic pressure-dependent, von Mises stress that yield should initiate close to the border of the contact for confinements, a/t, in the order of a few unities (figure 9(II)). Such a modified von Mises criterion is simply calculated by subtracting a linear pressure dependent term, αp_H, from the classical von Mises stress [28] (p_H is the hydrostatic pressure and α an empirical coefficient in the order of 0.2 for glassy polymers [28, 32, 33]). From figure 8, it is seen that the first yield deformation is experimentally found to occur within a confinement range (about 6-10) where the maximum modified von Mises stress is located near the periphery of the contact. The pressure dependence of the yield stress of polymer can therefore account for the localization of plastic deformation close to the edge of the contact in the case confined films.

4.2 *Elastic/Plastic Indentation Limit for Confined Polymer films*

The pressure dependence of polymer yield stress can further be considered to determine the normal load at the onset of yield within confined coated contacts. A simple dimensional analysis shows that the onset of yield within a coating can be completely defined as a function of two normalized parameters, t/R and $p_m=P/\pi a^2$. In figure 10, the experimental boundary between the elastic and plastic domain has been determined as a function of these two normalized parameters from a set of contact experiments using acrylate films with different thicknesses and spheres with various radii. For each experiment, the occurrence of plastic deformation was deduced from to the observation of a residual imprint after indentation. In the same graph, the theoretical boundary between elastic and plastic deformation has also been reported. The later was calculated using a modified pressure dependent von Mises criterion whose parameters where determined from independent constant strain rate compression experiments using bulk acrylate specimens. The strain rate of indentation experiments was ill-defined, but it was assumed to lie in the range 2.10^{-2} s^{-1}-2.10^{-4} s^{-1}. Within these uncertainties in the actual indentation strain rate, it turns out that the application of such a pressure dependent yield stress criterion can adequately describe the boundary between elastic and plastic indentation of confined polymer films. As shown in figure 10, this is obviously not the case for a simple von Mises criterion.

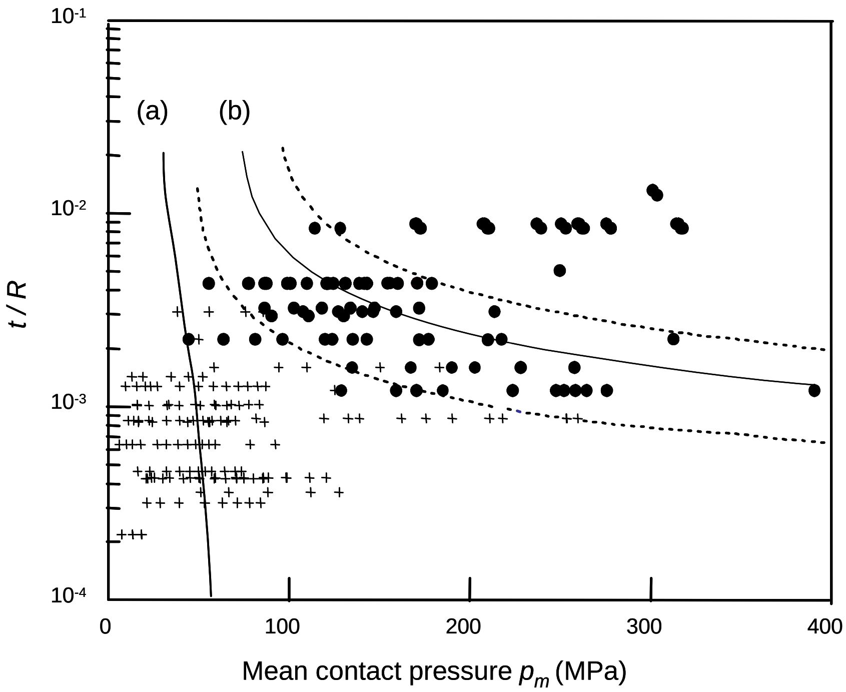

Fig. 10. Elastic and plastic indentation domains of acrylate films confined between glass substrates. (+) elastic response, no residual indentation imprint (●) plastic response as indicated by a residual contact imprint. Experiments were carried out using different film thicknesses, *t* (between 18 μm and 110 μm) and sphere radii, *R* (between 750 μm and 360 mm). (a) theoretical elastic limit calculated from a von Mises criterion using the bulk compression yield stress of the acrylate polymer at a 2.10^{-3} s^{-1} strain rate; (b) theoretical elastic limit calculated from a pressure dependent von Mises criterion at a strain rate of 2.10^{-3} s^{-1}. The lower and upper dotted lines correspond to the calculated elastic boundaries at strain rates equal to 2.10^{-4} and 2.10^{-2}, respectively.

5. Conclusions

Thin polymer films lying on rigid substrates are encountered in many tribological situations. We have shown that the high values of the hydrostatic pressure which develop in confined geometries – i.e. when the contact radius is larger than the film thickness - may significantly alter the mechanical properties of the polymer layer which in turn affects its tribological behaviour. These effects of confinement can be interpreted in the light of the well known pressure dependence of the mechanical properties of polymers. In this respect, viscoelastic properties are known to be thermally shifted by the hydrostatic pressure. This shift is experienced under *ordinary* contact conditions and may result in orders of magnitudes changes in the viscoelastic modulus. Conversely, contact techniques may help analysing the pressure-temperature superposition properties of the polymers, as other methods are technically difficult. Yield threshold is also known to be affected by the hydrostatic pressure. We show that confinement results in characteristic plastic imprints, which can be explained using a pressure dependent von Mises criterion. As a conclusion, it may be important to take into account the pressure dependence of the mechanical properties of the polymers in order to explain the tribological behaviour of substrates coated with polymers. For that purpose, the approximate oedometric contact model, recalled in the text may be helpful.

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