

Measurement of the Thickness of Coating Layers Using the Contact Resonance Technique with Fast Microprobes

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Introduction

The composite elastic modulus of a polymer coating on a solid substrate increases when the coating thickness is decreased. This is caused by the increasing influence of the modulus of the substrate. Hence, the measurement of the elastic modulus of a thin film permits to determine the thickness of the film. The advantage of such an indirect method is that it is non-destructive since it not necessary to scratch the film in order to measure the height difference between film and substrate. Yet, the dependence of the film elastic modulus on its thickness is not known theoretically and to date there is no universally accepted equation describing it. A well-established method to probe the elastic modulus with an AFM, which has been used to prove this correlation, is the recording of force distance curves (FDC). The elastic modulus of a coating layer probed by FDC depends on the relationship between deformation and film thickness. Several models and equations have been proposed, expressing the measured elastic modulus as a function of the moduli of the components, the layer thickness, the deformation, and various *ad-hoc* parameters [1]. Through a semi-empirical hyperbolic fit equation, the thickness of a polymer coating can be determined in the range 0-200 nm [2-4].

The change of the elastic modulus can also be accessed through the contact resonance frequency, which increases at higher moduli. This makes the contact resonance technique another candidate for thickness measurements [5].

Theory

If the system can be modeled as two springs with elastic constants k_s (sample) and k_c (cantilever) and can be described by Hertzian contact mechanics, the contact resonance frequency f_c in dependence of the free resonance frequency of the cantilever f_0 can be calculated by [5]:

$$f_c \cong \left[\frac{5}{4} \pi \frac{1}{\gamma x_0 L} \left(1 - \left(\frac{5}{12} \pi \right)^2 \frac{k_c}{\sqrt[3]{FRE_{tot}^2}} \right) \right]^2 f_0, \quad (1)$$

with the relative position of the tip on the cantilever γ , the wavenumber $x_0 L$ ($= 1.8751$ for the first flexural mode), the static force F , and the tip radius R . The reduced elastic modulus E_{tot} is defined as

$$\frac{1}{E_{tot}} = \frac{3}{4} \left(\frac{1-\nu^2}{E} + \frac{1-\nu_t^2}{E_t} \right), \quad (2)$$

with the Poisson's ratios of sample and tip ν and ν_t , and the elastic moduli of sample and tip E and E_t . For a silicon tip, $E_t = 160$ GPa, and $\nu_t = 0.28$. When f_c is determined for several static forces F , the data can be fitted with Eq. 1, with γ and E_{tot} being fit parameters.

Experimental Details

Sample Preparation

Contact resonance measurements were performed on films of polystyrene (PS, average $M_w \approx 280,000$), poly(methyl methacrylate) (PMMA, average $M_w \approx 120,000$), and poly(*n*-butyl methacrylate) (PnBMA, average $M_w \approx 337,000$). All experiments were conducted at room temperature. PnBMA has a broad glass transition around 15°C, so it is in the transition between glassy and rubbery state at room temperature. The glass transition temperatures of PS and PMMA are above 100°C, so they are in a glassy state at room temperature. The polymers were dissolved in toluene and then spin-coated onto glass substrates, previously cleaned and rinsed with toluene. The film thickness has been varied by diluting the spin coating solution. Films with a thickness above 400 nm are considered as bulk.

Experimental Setup

Experiments were conducted with a Cypher AFM (Asylum Research, Oxford Instruments, Santa Barbara, USA) with PPP-FMAuD cantilevers (elastic constant $k_c \approx 3$ N/m) from Nanosensors (NanoWorld, Neuchatel, Switzerland).

Cantilever calibration and tip characterization

Before the measurement, the sensitivity of the cantilever was determined by recording an FDC on an uncompliant surface, such as a silicon wafer. The elastic constant was determined through the thermal noise spectrum. The shape of the tip was characterized by scanning a TGT1 test grating (NT-MDT Spectrum Instruments, Moscow, Russia) consisting of an array of sharp tips. The resulting image is a replica of the tip.

Contact resonance frequency measurement

The contact resonance frequency can be measured either for a single point on the sample or through scanning techniques like the dual AC resonance tracking (DART) mode. In this mode, the tip contacts the sample at a static force, and then the cantilever performs oscillations at an amplitude which is much lower than the sample deformation to ensure permanent contact. Measurements have shown that scanning in DART mode on a polymer sample with an elastic modulus well below 10 GPa is problematic, because the tip is in contact with the sample throughout the whole scan. By scanning with high static forces, abrasion of the film was

observed. Scanning with a lower static force may lead to a characteristic ripple pattern. In both cases, the sample is altered during the measurements. This renders scanning contact resonance methods inappropriate to study polymer coatings. Because of the aforementioned shortcomings of scanning methods, the contact resonance frequency of polymer films was measured through frequency sweeps on single points. For each data point, six point-measurements have been conducted, each on a different spot on the sample, and averaged. The first flexural mode has been used in all measurements shown here.

Results

Figure 1 (taken from Ref. [5]) shows CR frequencies measured on PMMA films of different thickness through single point measurements. Additionally, frequencies on glass and on PS (bulk) are shown. The data are fitted with Eq. 1. The CR frequencies increase with decreasing film thickness because of the growing influence of the mechanical properties of the substrate. Assuming a Poisson's ratio of 0.4 for PMMA, the elastic moduli resulting from the fits are $E_{tot} = 9.4$ GPa ($E = 6.2$ GPa) for bulk, $E_{tot} = 11.5$ GPa ($E = 7.6$ GPa) for 100 nm, and $E_{tot} = 14.2$ GPa ($E = 9.5$ GPa) for the 45 nm film. Hence, it is possible to distinguish films of different thicknesses resulting in a modulus difference of ca. 1-2 GPa.

For comparison, the frequencies on glass are significantly higher. This is expected, as glass is known to be much stiffer than PMMA or PS. On glass, $E_{tot} = 62.3$ GPa ($E = 57.0$ GPa), and on PS, $E_{tot} = 7.2$ GPa ($E = 5.0$ GPa), with $\nu_{Glass} = 0.27$ and $\nu_{PS} = 0.33$.

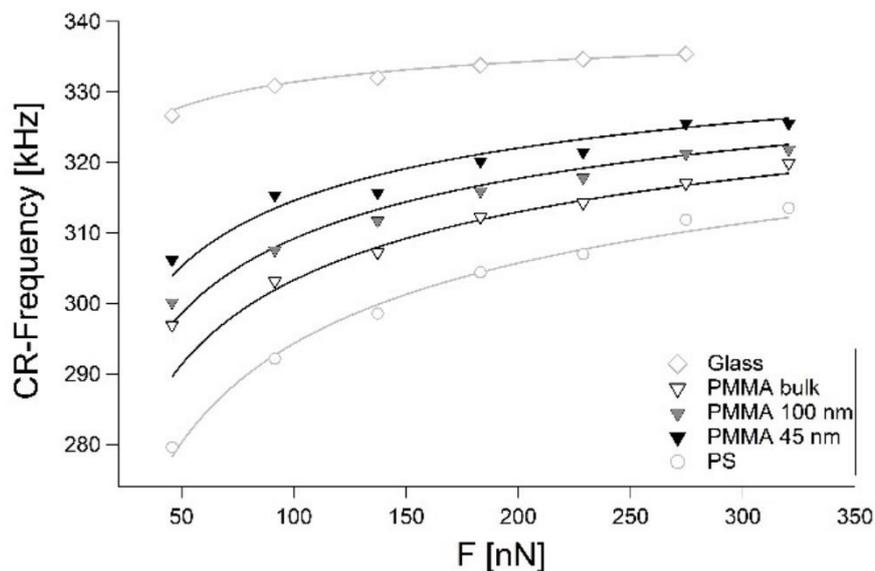


Fig. 1. CR frequencies measured for several static forces on glass, PS (bulk), and PMMA with varying film thickness. The data are fitted with Eq. 1. [5]

Discussion

Thickness resolution and comparison with FDC

As shown in Fig. 1, the difference in thickness that can be distinguished on a PMMA film is ca. 50 nm, corresponding to a difference in elastic modulus of ca. 1-2 GPa. The CR frequencies for different thicknesses are ca. 4 kHz apart. Data scattering is in the range of 1%, which is ca. 3 kHz. Such scattering would hardly allow for another curve with a thickness between 45 and 100 nm to fit in between. Therefore, a significantly better thickness resolution cannot be achieved with CR.

Assuming a relative measurement error of $\Delta f_c/f_0 = 1\%$, the uncertainty of the total elastic modulus ΔE_{tot} , i.e., the smallest difference in elastic modulus that can be detected by CR, can be calculated [5]. Figure 2 (taken from Ref. [5]) shows ΔE_{tot} for $\gamma = 0.97$, $F = 100$ nN, $R = 30$ nm, and four values of k_c (3, 10, 30, and 50 N/m). As expected, ΔE_{tot} increases with E_{tot} . For $k_c = 3$ N/m, $\Delta E_{tot} = 22$ GPa at $E_{tot} = 160$ GPa (14%), $\Delta E_{tot} = 4.2$ GPa at $E_{tot} = 60$ GPa (7%), and $\Delta E_{tot} = 0.03$ GPa at $E_{tot} = 3$ GPa (1%). The error ΔE_{tot} is inversely proportional to k_c and decreases sensibly with stiffer cantilevers. Yet, stiffer cantilevers are less suited for measurements on polymer samples, since they are likely to damage the sample.

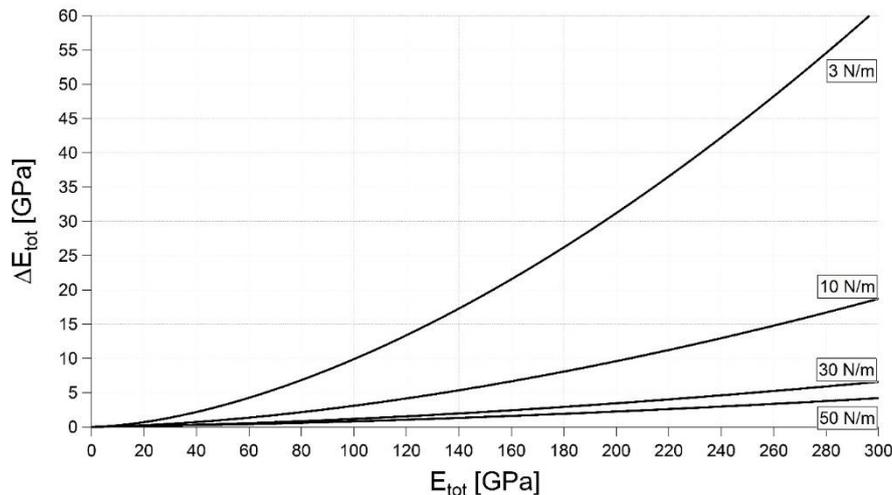


Fig. 2. Error ΔE_{tot} engendered by an uncertainty $\Delta f_c/f_0 = 1\%$ [5].

Compared to thickness measurements with FDC, the resolution of CR is significantly worse. FDCs allow a distinction of 6 different thickness values between 45 nm and bulk PMMA [4], whereas CR could hardly allow to distinct more than one value in this range, as shown in Fig. 1. Figure 3 (taken from Ref. [4]) shows deformation vs. deflection from FDCs on PMMA, together with the hyperbolic fit. CR measurements only allow to qualitatively discern films of different thickness, with a resolution that is much worse than that of the quantitative FDC analysis. An advantage of the CR technique is, however, that it also works for very stiff coatings. FDCs are only feasible up to moduli of several GPa, while CR can still be applied over 100 GPa.

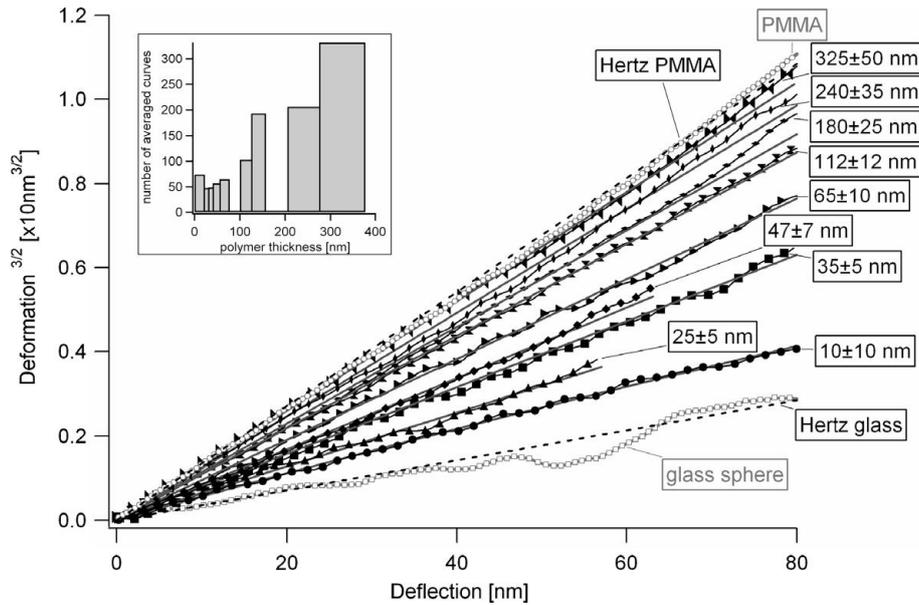


Fig. 3. Deformation vs. deflection curves of PMMA with varying thickness, together with hyperbolic fits for the thin films and Hertzian fits for the bulk PMMA and glass samples [4].

Soft samples

A counter-intuitive behavior is observed on PnBMA, which is in the transition between glassy and rubbery state and therefore less stiff than PS or PMMA, with E in the range of several 100 MPa. Figure 4 (taken from Ref. [5]) shows the CR frequency on a single point recorded over time while the tip is constantly pushed against the sample with a force F for two different forces on PnBMA films with varying thickness, as well as on glass for comparison. Although thin films are stiffer because of the influence of the substrate, a higher CR frequency is observed for thicker films for $F = 130$ nN. The frequency increases over time because the tip indents the soft polymer more and more over time. Thereby, the contact area between tip and polymer increases, which leads to an increase in the CR frequency. This also explains the higher frequency for thicker films: the tip can indent the sample more, and the contact area is larger than for thinner films. This effect is stronger than the stiffening of the sample caused by the substrate for thin films. For the lower static force ($F = 32$ nN), the frequency is lower for the thicker film at the beginning, as expected. After 80 s, however, more polymer surrounds the tip and the contact area becomes so large that the frequency surpasses the frequency on the 25 nm film.

This effect shows that the qualitative thickness determination via CR is only possible on glassy films and leads to erroneous results for softer films with high deformations.

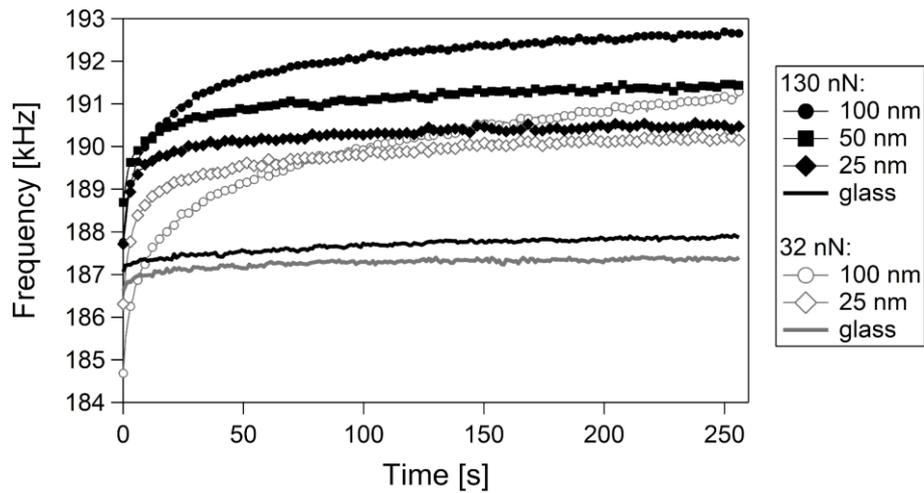


Fig. 4. CR frequency over time on PnBMA and glass for two different values of the static force F [5].

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