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Film thickness limits of a buckling-based method to determine mechanical properties of polymer coatings

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Abstract

Characterizing the mechanical properties of polymer coatings typically requires access to specialty equipment, the analysis through which can be tedious despite instrumental precision. An alternative method reported in the literature, strain-induced elastic buckling instability for mechanical measurements (SIEBIMM), is a high throughput, facile yet accurate method, used to characterize the Young's modulus of supported films and coatings. SIEBIMM can easily be implemented in both academic and industrial settings.

Hypothesis. We hypothesize that the SIEBIMM method has an upper coating thickness limit beyond which the assumptions and practicality of the method are no longer valid.

Experiments. The Young's moduli of model polyvinyl alcohol coatings (on polydimethylsiloxane substrates) with thicknesses ranging from 67 nm to 40 μm were determined using the SIEBIMM method and the data were subjected to a rigorous statistical analysis.

Findings. SIEBIMM could accurately characterize coatings up to 35 μm thick. The Young's modulus of all coatings $\leq 35 \mu\text{m}$ was $1.6 \pm 0.1 \text{ GPa}$ at 50% RH, which agreed with free-standing polyvinyl alcohol films measured by traditional tensile testing. For the method to be used on thicker coatings, it is essential to consistently measure coating thickness and buckling wavelength at the same location to minimize potential error.

Keywords: SIEBIMM, polymer coatings, PVOH, Young's modulus, mechanical properties

1. Introduction

Advancements in functional materials have brought with them the need to develop coatings durable enough to withstand a wide array of external stresses. Coatings in advanced applications such as sensors, flexible and stretchable electronics, and energy storage devices, and in more conventional construction, furniture, food, plastics, paper/board applications often require the ability to tolerate changes in environmental humidity, be abrasion resistant and demonstrate excellent shape retention. The Young's modulus, or the measure of stiffness (or elasticity), of a material is an important mechanical property to determine its suitability as a coating. In this work, model polyvinyl alcohol (PVOH) coatings were used to investigate the limitations of a buckling-based method, namely strain-induced elastic buckling instability for mechanical measurements (SIEBIMM) [1], to determine the Young's modulus as a function of polymer coating thickness. While SIEBIMM has been implemented in academic settings to characterize polymer thin films up to 1.7 μm thick [1–9], no accounts exist which systematically probe the limitations of the technique with respect to film thickness – a key parameter in the design and optimization of polymer coatings. In fact, the literature available on using the SIEBIMM method to characterize polymeric coatings is sorely lacking. Extending facile and accessible, yet highly accurate characterization techniques, such as SIEBIMM, to thick polymer coatings would also encourage their use in industrial settings, where access to specialty equipment is often limited.

Despite the fact that conventional methods such as dynamic mechanical analysis (DMA) [10] and tensile testing are widely used to determine the Young's modulus of polymer films, they require the use of freestanding samples, and as such are not applicable to coatings supported by an underlying substrate. Though some thick coatings can be removed from their substrate, many cannot. Most importantly, however, while analyses of free-standing films is typically more straightforward, such films are likely not representative of how a given material will behave when supported by a substrate. To circumvent this issue, the mechanical property of coatings can be assessed using, for example, three point bending [11] and indentation tests with an atomic force microscope [12], or through nanoindentation [13] or micro-scratch [14] experiments. Nonetheless, although these techniques offer high precision, they are often tedious, and require an expert skill set and access to highly specialized equipment. Conversely, buckling-based

mechanical testing, such as SIEBIMM used here, is a high throughput, and facile yet precise method by which to characterize the mechanical properties of supported coatings [1–8]. The comparison of the key differences between SIEBIMM and the more conventional mechanical testing methods in Table 1 further underlines the motivation to investigate the thickness limitations of the SIEBIMM method using a model system in order to understand its viability for a broad spectrum of polymers.

The basic principle of this buckling-based method is to measure the way in which a relatively thin, rigid film wrinkles when the soft substrate upon which it is coated is compressed. The buckling instability, defined as the balance between the energy required to bend the stiff upper film and the energy required to deform the soft underlying substrate, leads to a minimum wrinkle wavelength, which minimizes the total strain energy in the system [1]. The wavelength of the wrinkles depends on the properties of both the substrate and the film, leading to a unique buckling pattern first observed by Biot, who modeled the bending of an infinite beam on an elastic substrate [15]. Later, Bowden et al. observed ordered structures in thin metal (gold) films deposited on polydimethylsiloxane (PDMS) [16]. Bowden's work also established a mathematical formula linking the buckling wavelength to the Young's modulus of the film that takes into account the thickness of the film, the Young's modulus of the substrate and the Poisson's ratios of both the film and the substrate. This formula was later used by Stafford and co-workers who, for the first time, implemented this buckling-based method with polymeric thin films, introducing the SIEBIMM method and name [1,3]. In recent years, the SIEBIMM method has been used to determine the Young's modulus of polymers films [1,3,17,18], liquid crystal elastomers [19], biopolymers [20], membranes [21,22], polymer brushes [6] and numerous polymer multilayer thin-film composites [23–27], including those with nanoparticles such as, cellulose nanofibrils [28–30], and cellulose nanocrystals [9,31], demonstrating its applicability to a variety of polymeric and colloidal systems.

Until now, the Young's modulus of supported thin films/coatings has been characterized using SIEBIMM for film thicknesses ranging from tens of nanometers up to 1.7 μm [9], generally concluding that within this range the modulus is constant. However, commercial coatings are typically several to tens of micrometers thick (but not necessarily possible to be made free-standing), and the upper limit for the SIEBIMM method in terms of thickness remains unclear. Whilst the mechanism of buckling in itself has no thickness limit, the SIEBIMM method

imposes a strict set of boundaries (discussed in the Results and Discussion Section), beyond which the method becomes unreliable for mechanical testing [1]. Additionally, delamination of thick coatings may preferentially occur before uniform wrinkling, introducing a practical limit to the method. Here, we demonstrate the coating thickness limits of the SIEBIMM method using model PVOH films deposited on PDMS substrates, ensuring that all of the conditions of the method are met; the adaptability of this method for the characterization of micrometer-thick polymer films is assessed. Overall, we found that the SIEBIMM method could be reproducibly applied to model PVOH coatings of up to 35 μm , and provided an accurate modulus with reasonable precision. Precision could be further improved following some straightforward recommendations to overcome film inhomogeneities. Though the limitations in coating thickness demonstrated here are PVOH specific, we believe that the SIEBIMM method could be reliably implemented to assess the mechanical properties of micrometer thick coatings from a variety of specialty and commercial polymers. The comprehensive analysis of the limitations of the mechanical testing method shown in this work, is the first of its kind in regards to SIEBIMM, and will be a useful tool for those looking to extend their portfolio of coating characterization techniques.

Table 1. Comparison of the key differences between polymer film mechanical testing methods highlighting their measured mechanical property, limitations, necessity for specialty equipment and their cost.

	Measurement technique	Sample thickness range	Measured mechanical property	Surface roughness sensitivity	Main limitations	Specialty equipment?	Cost
FREESTANDING	Dynamic mechanical analysis	0.02 – 10 mm	Storage modulus	Low	Requires accurate master curve (calibration)	Yes	\$\$\$
	Tensile testing	μm - cm	Tensile modulus	Low	Requires accurate measurement of sample dimensions	Yes	\$\$
	Bending tests	μm – cm	Flexural modulus	Low	Requires accurate measurement of sample dimensions	Yes	\$\$
COATINGS	Nanoindentation	Min. 10 \times indentation depth	Elastic modulus	High	Limited lateral resolution, Substrate effects, tip dependence	Yes	\$\$\$
	SIEBIMM	40 nm – 35 μm	Young's modulus	Moderate	Film thickness heterogeneities	No*	\$
	Atomic force microscope indentation	nm – a few μm	Elastic modulus	High	Surface adhesion, tip contamination	Yes	\$\$\$

	Atomic force microscope three-point bending	nm - μm	Young's modulus	High	Tedious, surface adhesion, tip contamination	Yes	\$\$\$
	Micro-scratch testing	μm - mm	Hardness	Moderate	Substrate effects, tip contamination	Yes	\$\$\$

* SIEBIMM does require specialty equipment to measure coating thickness, such as ellipsometry, profilometry, SEM (edge measurement), AFM (scratch height analysis) or a small-angle light scattering setup [1].

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVOH). The PVOH used was a mixture of a high molecular weight (M_w) PVOH (Mowiol® 28-99, 145 000 g mol^{-1} , Sigma Aldrich) and a low M_w PVOH (Mowiol® 6-98, 47 000 g mol^{-1} , Sigma Aldrich) at a 2 to 1 mass ratio, respectively. A 5 wt% PVOH stock solution was prepared by dissolving the polymer mixture into distilled water at 90°C under constant stirring for minimum 2 h to ensure complete dissolution. The stock solution was then stored at room temperature.

Polydimethylsiloxane (PDMS). PDMS was purchased from Sigma Aldrich (Sylgard® 184, 10 g clip-pack). The Sylgard elastomer kit was comprised of a base and a curing agent.

2.2. Methods

PDMS substrate preparation. PDMS substrates were prepared by mixing the base and the curing reagent using a mass ratio of 10:1, respectively. The mixture was vigorously mixed by hand for 10 min to obtain a homogeneous mixture, and then kept under vacuum for at least 1 hour to remove any trapped air. The PDMS was cast into a 5 cm \times 5 cm metallic mold (polished to avoid defects on the surface) and subjected to vacuum for an additional 30 min. Finally, the PDMS was cured at 100°C for 1 h. After cooling, the 4 mm thick PDMS was cut into 5 cm \times 1 cm strips and rinsed with distilled water and ethanol. The thickness of the PDMS strips was measured using a digital caliper.

Dynamic mechanical analysis (DMA) of PDMS. The Young's modulus of PDMS was determined using RSA3 DMA (TA instruments, New Castle, DE, USA). PDMS samples (1 cm \times 3 cm by 4 mm thick) were compressed using a compression rate of 0.6 mm min^{-1} , a preload of 1

N, with a 15 mm gap between the clamps. The Young's modulus varied between 4.5 and 6.8 MPa, depending on the batch of PDMS – the exact Young's modulus measured by DMA for each PDMS batch was used in the respective calculations. These values of Young's modulus are in the same range as those reported in the literature [9,28,31]. A Poisson's ratio of 0.5, a typical value for elastomeric materials, was assumed for PDMS [1].

PVOH films and coatings. Freestanding PVOH films (for tensile test measurements) with a 50 g m⁻² basis weight were prepared by solvent casting from aqueous solution. The 5 wt% stock solution of PVOH was cooled in a polytetrafluoroethylene mold and dried at 23 °C and 50% relative humidity (RH) for one week. PVOH coatings were also solvent cast onto the PDMS substrate surface. Prior to coating, a corona treatment (4 passes under 300 mA, Calvatron SG-2) was performed on the PDMS substrate in order to increase its surface energy, and promote adhesion between the PVOH coating and the substrate (without a corona treatment, PVOH does not wet the hydrophobic PDMS surface). In a corona treatment, a corona discharge plasma is generated by applying a high voltage to an electrode, which then oxidizes the PDMS surface and causes a change in the surface properties, namely the surface energy, of the PDMS. This treatment forms a ca. 1 nm thick SiO₂ layer at the substrate/air interface, which then rapidly dissipates in to the bulk PDMS [32,33], and as such does not affect mechanical properties of the PVOH coatings. PVOH coatings of varying thicknesses (ranging from 67 nm to 40 μm) were prepared by solvent casting 300 μL of PVOH solutions with ranging concentrations (0.01 to 2.5 wt%) onto the PDMS substrate surfaces (immediately, within minutes, following the corona treatment) and subsequently drying the coatings under ambient conditions (50% RH and 23°C) for 48 hours.

Tensile tests for freestanding PVOH films. Tensile tests (Instron 5965, Norwood, MA, USA) were performed on cast PVOH films (5 cm × 1.5 cm) using a crosshead speed of 10 mm min⁻¹. Each film was conditioned at 23 °C and 50% RH for at least 48 hours before testing and five repetitions were performed on three separate films.

PVOH coating thickness measurements. Coating thickness is a sensitive parameter, and small variations can induce significant fluctuations in the Young's modulus calculations from SIEBIMM. Two separate methods were used to measure coating thickness as a function of humidity. Spectroscopic ellipsometry (SE) was used to measure the coating thickness in ambient humidity (40-55% RH) and at 0% RH. As the thicker PVOH films are beyond the conventional

limits of film thickness for SE, the values obtained for coating thickness were also compared to those obtained by scanning electron microscopy (SEM), carried out at 0% RH. Both SE and SEM provided the same coating thicknesses regardless of relative humidity (ambient or 0% RH). As a result, to attain a statistically valid set of data, PVOH film thicknesses presented here are an average of values determined by both SE and SEM (see Supporting Information, Table S1 for standard deviation and coefficient of variance in film thickness). A more detailed description of each of these two methods can be found below.

Spectroscopic ellipsometry (SE). To accurately measure the difference in film thickness between 0% RH and ambient humidity (40-55% RH), a M-2000UTTM variable angle spectroscopic ellipsometer (J.A. Woollam Co., Inc, Lincoln, NE, USA) was used, with wavelengths between 250 and 1680 nm, and incident angles of 55 – 75° using 5° increments. 0% RH was achieved by purging a sealed heating stage with dry N₂ gas and subsequently conducting the measurement through the heating stage. CompleteEase[®] software was used to determine the thicknesses of the nanocomposite coatings, using a classic Cauchy model to fit the raw ellipsometry data, assuming the PVOH coating was a transparent film.

Scanning electron microscopy (SEM). SEM imaging of PVOH coated slices of PDMS (carefully cut to size with a razor blade) was performed using an environmental scanning SEM (ESEM) in EDT mode (Quanta 200©, FEI, Japan) at a working distance of 10 mm with 10 keV and a spot size of 3.5 nm. Prior to imaging, the samples were gold sputter coated (5 nm thick gold coating). At least 5 images were taken per magnification. ImageJ software (U. S. National Institutes of Health, Bethesda, Maryland, USA, <https://imagej.nih.gov/ij/>) was used to determine the coating thickness. A minimum of 20 analyses were performed for each image ($N=100$).

Strain-induced elastic buckling instability for mechanical measurements (SIEBIMM). After deposition of the coating onto the PDMS substrate and subsequent drying, the samples were conditioned at 23°C and 50% RH overnight prior to performing buckling measurements. For these measurements, the coated PDMS substrates were fixed with screw clamps to a homebuilt compression apparatus (Figure 1A) [9], and compressed at 1 mm min⁻¹ to a final compression strain of 5% (Figure 1B). The speed and degree of compression were controlled using the gauge on the compression apparatus and the compression dial. Once a compression strain of 5% (i.e. a decrease of 5% in sample length) was achieved, the buckling pattern was imaged using a USB optical microscope (Figure 1C). The observed buckling pattern is a result of the dissipation of

strain in the PVOH coating caused by the deformation of the elastomeric PDMS substrate. It should be noted that within the elastic region, the rate of compression does not have an effect on the wavelength of the buckles; however, a decreased compression rate minimizes cracking of the coating. Previous work in our lab supports this as a suitable rate. It is also important to mention that when the samples are removed from the strain device, the buckles relax completely back to a flat film (within a few minutes), see Supporting Information, Figure S1A. As such, it is not entirely necessary to use a compression apparatus, such as the one used here (Figure 1A), to carry out SIEBIMM measurements. In fact, compression can be carried out by carefully wedging the coated PDMS substrate between any two stationary objects at a predetermined distance from one another (at 95% of the sample length for a 5% compression, for example).

Experiments were carried out in a climate-controlled room (23°C and 50% RH). The Young's modulus of each coating was calculated using Equation 1:

$$E_f = 3E_s \frac{(1 - \nu_f^2)}{(1 - \nu_s^2)} \left(\frac{\lambda}{2\pi d_f} \right)^3 \quad \text{Eq. 1}$$

Where E_f is the Young's modulus of the PVOH coating, λ is the wavelength of the periodic wrinkles induced in the coating upon buckling, E_s is the Young's modulus of the PDMS substrate, ν_s is the Poisson's ratio of the substrate, ν_f is the Poisson's ratio of the coating (assumed to be 0.33) [1], and d_f is the coating thickness.

Wavelength and amplitude measurement. Buckling patterns were imaged using a USB optical microscopy with a focal range from 10 mm to 500 mm, 5 M pixels image sensor and 10x to 300x magnification ratio (Figure 1C), and the wavelengths of the buckles were analyzed using an open source image analysis software (ImageJ). Between 20 and 90 wavelengths were measured per sample. The amplitude of the buckled coatings was measured using an InfiniteFocus optical profilometer (Bruker Alicona, Raaba/Graz, Austria) with a vertical resolution of 1.6 μm and a lateral resolution of 5.8 μm on image of 2.2 mm \times 7.5 mm (Figure 1D).

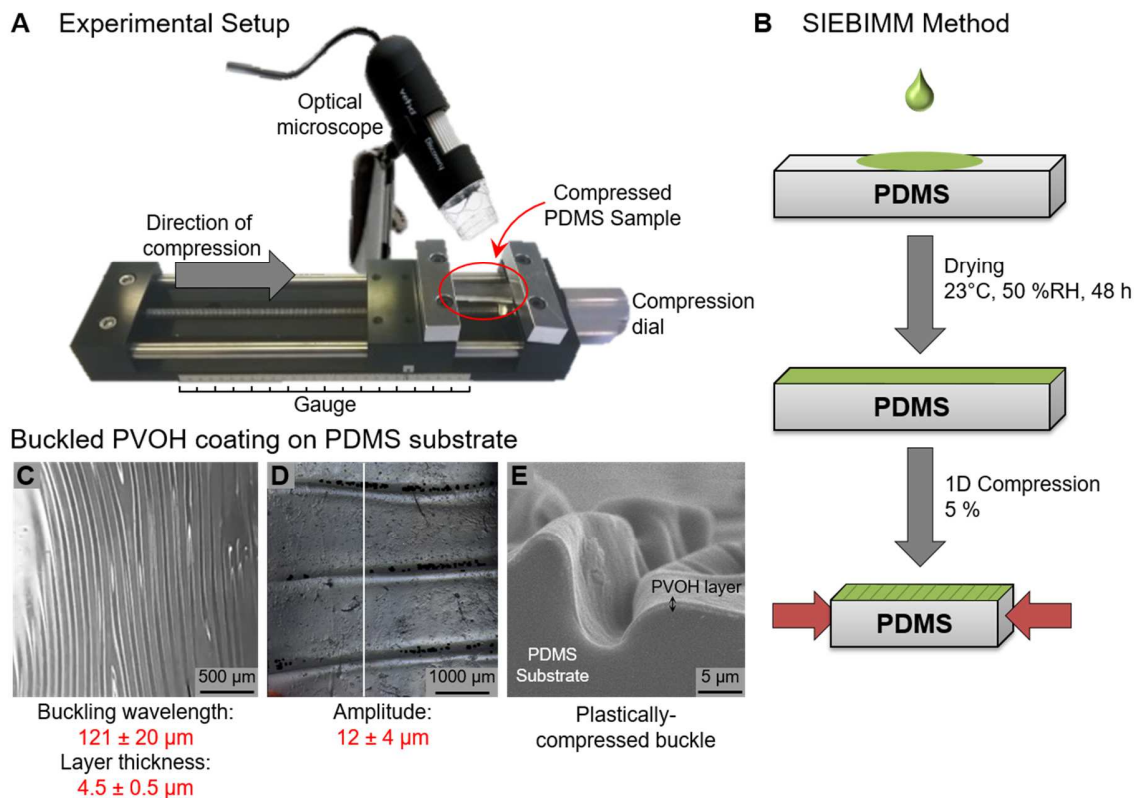


Figure 1. A) Photograph of the experimental setup used to perform buckling measurements using a homebuilt compression apparatus and a USB optical microscope and B) a schematic of the preparation of a PVOH coating on a PDMS substrate, and subsequent buckling and buckling patterns of micrometer-thick nanocomposite coatings. Along with C) buckling wavelength captured using a USB optical microscope, C) amplitude measured using an optical profilometer, and D) plastically compressed (i.e., over-compressed) buckle imaged using SEM.

3. Results and Discussion

3.1. Validity of SIEBIMM conditions for thick coatings

PVOH coatings of various thicknesses (ranging from 67 nm to 40 μm) were used as model coatings to assess the applicability of the SIEBIMM method to characterize the mechanical properties of coatings above 1.7 μm , which is the thickest coating measured by SIEBIMM in the literature [9]. While PVOH as a model system is not able to predict the SIEBIMM suitability of all synthetic polymers, it represents a class of widely used polymers with similar Young's

moduli and Poisson's ratios, including, e.g., polypropylene, Nylon 6 and high-density polyethylene (Table 2) [34,35].

Table 2. Commercially available and widely used polymers (ordered alphabetically) with similar Young's moduli and Poisson's ratios to polyvinyl alcohol (used in this work).

	Tensile (Young's) Modulus GPa [35]	Poisson's ratio [34]
Polycaprolactam (Nylon 6)	1.58 – 3.80	0.42
Polycarbonate	2.38	0.41
Polyethylene (high density)	1.06 – 1.09	0.46
Poly(methyl methacrylate)	2.24 – 3.24	0.36
Polyphenyl sulfone	2.29 – 2.4	0.37
Polypropylene	1.14 – 1.55	0.43
Polystyrene	2.28 – 3.28	0.35
Polyvinyl alcohol	1.2 ± 0.3*	0.33
Poly(vinyl chloride)	2.4 – 4.1	0.40

* As measured by DMA

First, we evaluated whether it was valid to use Equation 1 with our experimental setup. The five main conditions that must be satisfied to calculate the Young's modulus of supported coatings using SIEBIMM, are as follows: i) applied compression strains must be small ($\epsilon \ll 10\%$) and result in buckled films with sinusoidal waveforms, ii) the amplitude of the wave pattern must be smaller than the wavelength, iii) the width of the coating layer must be significantly greater than its thickness, iv) the elastic modulus of the layer must be much higher than that of the substrate, and v) the substrate thickness must be much greater than the layer thickness [1]. We believe that all conditions were met given that compression was constant at 5% and sinusoidal patterns were observed (Figure 1C), the amplitude and wavelength of the buckles did not exceed 31 and 945 μm , respectively, the PDMS strips were 4 cm \times 1 cm and 4 mm thick, the modulus of the substrate was in the MPa range and that of PVOH in the GPa range, and the thickest PVOH coating was 40 μm ; these results and other potential limitations are discussed in detail below.

We identified that a possible obstacle in applying SIEBIMM to micrometer-thick coatings is ensuring that the films buckle throughout their entire thickness and do not crack or delaminate from the substrate. As shown by the SEM image in Figure 1E, for coating thicknesses up to 35

μm , this is indeed the case. In fact, even after the onset of plastic deformation ($\epsilon \approx 20\%$ followed by release of strain), SEM images show a complete buckling of the PVOH coating (Supporting Information, Figure S1B). These SEM images also revealed that the adhesion between the coating and the substrate was sufficient to avoid delamination or relaxation of the buckled patterns for PVOH coatings up to $35\ \mu\text{m}$ thick. Furthermore, when coatings were “over” compressed up to 25% strain, the buckling wavelength remained constant (data not shown), confirming good adhesion of PVOH to the PDMS substrate regardless of coating thickness. This is partially attributed to the PDMS corona treatment applied prior to coating which increases the hydrophilicity of the substrate and compatibility with PVOH. However, it should be noted that the substrate must be coated immediately (within minutes) following the corona treatment as the changes in surface energy are stable only within a narrow time frame due to the high mobility of siloxanes [32,33]. Finally, no cracking of the layer was observed (even for coatings thicker than $35\ \mu\text{m}$). While not observed here, in other polymer/nanoparticle thick coatings we have seen significant delamination and even complete detachment of the film from the substrate; the SIEBIMM user is warned to watch for this as it is apparent by eye and would obviously invalidate the use of Equation 1.

Upon unidirectional compression (at 5% strain), coatings up to $35\ \mu\text{m}$ buckled reversibly and reproducibly (independent of number of compression cycles), giving sinusoidal wave patterns as shown in Figure 2A, 2B and 2C for 4.5 , 16 and $35\ \mu\text{m}$ thick films, respectively, again meeting the first condition for Equation 1. Moreover, the buckling patterns remained stable as long as compression was maintained, regardless of the rapid relaxation potential of PDMS. An increase in thickness beyond $35\ \mu\text{m}$ resulted in films that were too rigid to be compressed into a homogeneous buckling pattern (Figure 2D). For all coatings up to $35\ \mu\text{m}$, the amplitude of the wrinkles (as observed through optical profilometry, Figure 2 inset values) was smaller than their wavelengths, fulfilling the second condition. As such, we conclude that the threshold for successfully using the SIEBIMM method to characterize the mechanical properties of these model PVOH films is between a coating thickness of 35 and $40\ \mu\text{m}$. Most importantly, demonstrated here is evidence that SIEBIMM can reliably be applied to relatively thick polymer films, particularly for those whose mechanical properties are similar to PVOH.

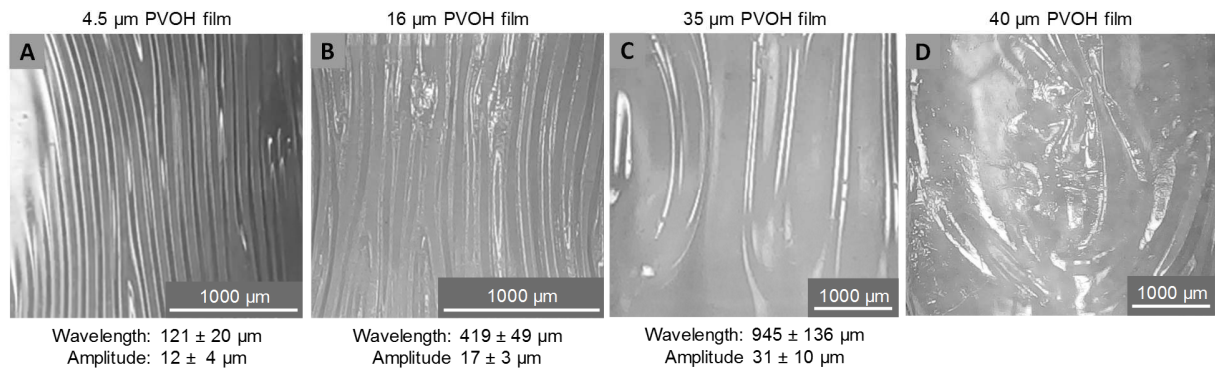


Figure 2. Optical micrographs of buckling patterns of PVOH coating of various thicknesses A) 4.5 μm , B) 16 μm , C) 35 μm and D) 40 μm on PDMS substrates elastically compressed to 5% compression strain. The wavelength and amplitude values for each buckling pattern are also shown as measured by the digital analysis of the micrographs and optical profilometry, respectively.

3.2. Effect of coating thickness on buckling wavelength

The buckling wavelengths measured for six coatings of varying thickness are shown in Figure 3A. A linear correlation was seen between the wrinkle wavelength and the PVOH coating thickness, for 67 nm to 35 μm thick coatings (regression coefficient $R^2 = 0.9996$). This correlation of wavelength with thickness agrees with that originally demonstrated by Bowden et al. [16], as well as subsequent users of buckling-based methods [1–8]. In Figure 3B, the standard deviation (absolute dispersion) and coefficient of variation (relative dispersion) of the buckling wavelengths are reported as a function of PVOH coating thickness. Absolute dispersion increases linearly with thickness, implying that sample heterogeneities increase with increasing thickness. Relative dispersion, on the other hand, shows a different trend; beyond a thickness of 1.9 μm , the coefficients of variation lie between 10 and 20% whereas the nanometer thick coatings show higher values due to the resolution/contrast limitations of the microscopes used (optical microscope and SEM). Regardless, the plateau in the coefficient of variation (at ca. 15%) indicates an acceptable set of data for buckling wavelengths up to a coating thickness of 35 μm . To ensure that the effect of thickness variation on buckling wavelength is minimized, we recommend that both thickness of the coating and the buckling pattern wavelength be measured at the same location on the sample. This statistical analysis also suggests that for thinner films,

higher resolution imaging is important for precise wavelength/modulus values, which is not necessary for thicker films.

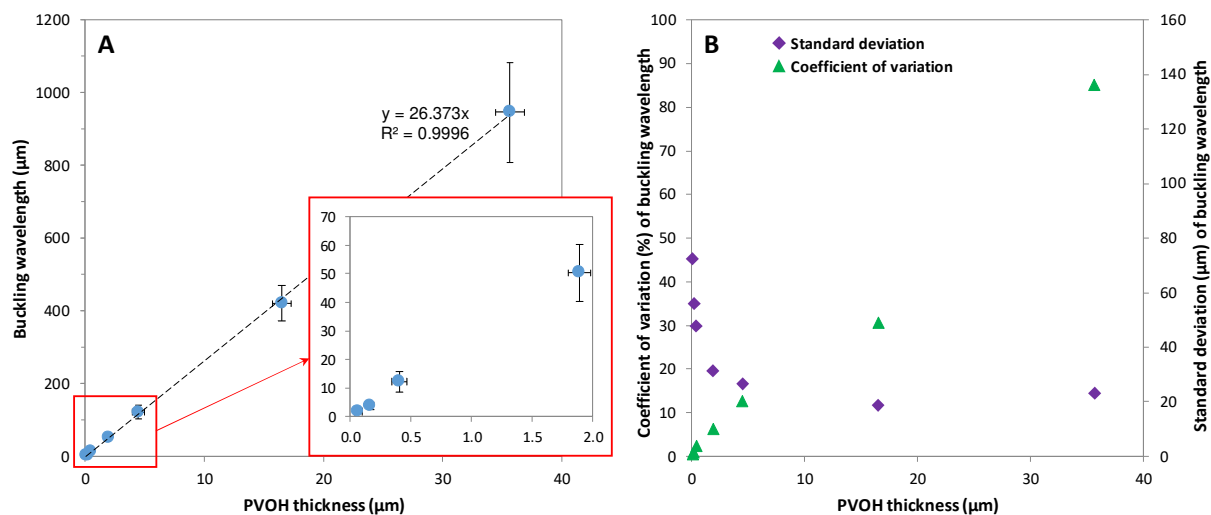


Figure 3. A) Buckling wavelength for PVOH coatings (measured at 50% RH) with different thicknesses prepared on PDMS by solvent casting and drying at ambient temperature (confidence intervals/error bars are the standard deviation of the mean) (inset to show buckling wavelength as a function of PVOH thicknesses under 2 μm), and B) absolute and relative dispersion of buckling wavelength values as a function of coating thickness.

3.3. Young's moduli of thick PVOH coatings through SIEBIMM

The Young's moduli for the PVOH coatings are shown in the box plot in Figure 4A where the red crosses represent the average value, and the horizontal line represents the median value. The lower and upper limits of the boxes are the first and third quartiles, respectively (50% of the central data lies between these two limits; 25% above and 25% below). For each box, any data located below or above the lower and upper ends of the chart whiskers, respectively, can be considered outliers (as shown by the black data points, which are the maximum values calculated for Young's modulus for the PVOH coatings).

The average values for the Young's modulus of the PVOH coatings are all between 1.2 and 2.5 GPa regardless of thickness (up to 35 μm). For PVOH coating thicknesses between 67 nm and 4.5 μm, the Young's moduli exhibit some anomalies, however, these are no longer present in

the coatings with thicknesses between 4.5 and 35 μm . Furthermore, at the largest thicknesses, the average and median values for Young's moduli are equal and variability is low. These results further support that the variations in the thinner coatings are more likely due to the lack of resolution in the microscopy techniques, and are not a reflection of the adaptability of the SIEBIMM method to micrometer-thick coatings.

An analysis of variance (ANOVA) test was performed in order to determine whether coating thickness has a significant impact on elastic modulus. For each film thickness, between 20 and 90 values of buckling wavelength were measured and an equal number of Young's moduli were calculated. Two hypotheses were formulated: the null hypothesis states that there is no influence of thickness on Young's modulus and the alternative hypothesis states that the thickness is an explicative value for Young's modulus. The bar chart of standardized coefficients (Figure 4B) is used to visually compare the relative impact of the thickness; the higher the absolute value of the coefficient, the more significant the effect of thickness on Young's modulus. Furthermore, when the confidence interval spans $x=0$, the difference between each group of values is considered insignificant. The group of values obtained with the lowest thickness ($d_f = 67 \text{ nm}$) was considered as a reference. Note that except for the second group ($d_f = 170 \text{ nm}$), all the other groups of data showed statistically insignificant differences. As such, we conclude that the values of the Young's modulus obtained for the thickest (35 μm) and the thinnest (67 nm) coatings are not significantly different. This further confirms the validity of the SIEBIMM method in characterizing micrometer thick coatings.

The average Young's modulus for PVOH coatings from all of the sets of data (independent of thickness) with propagated error is $2 \pm 2 \text{ GPa}$. To overcome the high sensitivity of the model to sample heterogeneities, a linear regression between wavelength and thickness values was performed as shown in Figure 3A. With this adjustment in the wavelength (i.e., using wavelength values from the linear equation shown in Figure 3A), a constant Young's modulus of $1.6 \pm 0.1 \text{ GPa}$ was obtained, which correlates well with a solvent cast PVOH film measured by more traditional tensile testing ($1.2 \pm 0.3 \text{ GPa}$ from DMA); three orders of magnitude higher than that measured for the PDMS substrate – again we emphasize that these values meet the fourth condition for Equation 1. This result indicates that a free-standing film and a thick coating have similar mechanical properties and that the substrate effect on these thicker coatings is negligible.

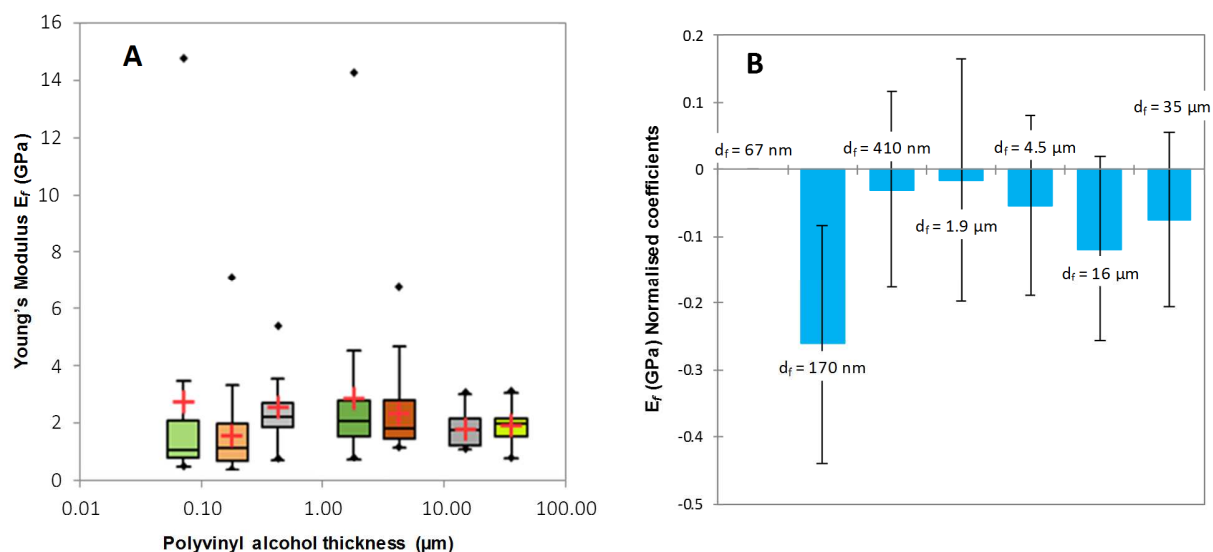


Figure 4. A) Box plot showing the Young's moduli for PVOH coatings calculated using the SIEBIMM measurements at 50% RH (where the black data points represent the maximum (or outlier) values obtained) and B) standardized coefficients (95% confidence interval). ANOVA study where explicative variable is thickness (from SEM), measured variable is Young's modulus, E_f (GPa).

3.4. Considerations for using SIEBIMM with thick polymer coatings

Whilst it is demonstrated here that all of the conditions required for the successful application of the SIEBIMM method are met in coatings up to 35 μm , there are a number of factors, which should be taken in to consideration when applying this method to thick coatings. Firstly, it is important to ensure that the sample geometries meet the conditions of the method; the width of the coating layer must be significantly greater than its thickness (condition iii) and that the substrate thickness must be much greater than the layer thickness (condition v), as they are here. These geometries are of course somewhat relative, however, a constant Young's modulus, independent of coating thickness, will indicate that these conditions are also fulfilled. Additionally, it is of vital importance to confirm good adhesion between the PDMS substrate and the polymer coating, and to ensure that the coating buckles throughout its entirety using, for example, SEM. Most importantly, in order to prevent the significant variations in Young's modulus that result from sample heterogeneities, both the film thickness and buckling wavelength must be measured at the exact same location on the sample. Using at least three different PVOH thicknesses in the micrometer range and fitting a linear trend to the plot of

buckling wavelength versus coating thickness allows for the most reliable values and a decreased standard deviation. To obtain the most relevant and precise Young's moduli, SIEBIMM should be applied to the coating thickness range of interest, aiming on the side of thinner films whenever possible (because sample heterogeneity and buckling wavelength error are smallest for thin films). For very thick coatings, a wider range of film thicknesses (and more data in the thin film regime) will also decrease the standard deviation. In all cases, one must ensure that all of the conditions of the method are being met for each of the chosen coating thicknesses.

4. Conclusions

This work investigated the adaptability of the buckling-based SIEBIMM method to determine the Young's modulus of micrometer-thick model polymer coatings. While buckling in itself does not have an upper thickness limit, it was hypothesized that the validity of the conditions of SIEBIMM must have an upper limit due to the decreased wavelength homogeneity of thicker, buckled coatings (Figure 2D). Young's moduli could be determined for PVOH coatings of up to 35 μm thick, whilst still meeting all of the conditions set forth by the model. To our knowledge, this is the first account of the SIEBIMM method being used to characterize such thick polymer coatings, and to provide a comprehensive analysis on the upper limits of the method. Previous reports utilizing SIEBIMM have only been applied to polymer coatings with a maximum thickness of 1.7 μm [9]. Evidence for the applicability of the SIEBIMM method to thick coatings – as provided by this study – greatly broadens its potential from thin film characterization at the laboratory scale, to providing an excellent tool to control and optimize industrially relevant coatings. One could even argue that this method could be utilized as a potential diagnostic tool for coating uniformity, in addition to its original purpose of determining the Young's moduli of polymer coatings. Although the data shown here pertain to the coating thickness limits of model PVOH coatings, it is apparent that the SIEBIMM technique could easily be applied to polymers such as polypropylene, Nylon 6 and high-density polyethylene which have very similar mechanical properties [34,35].

In order to validate the results shown here, a comparison was made to literature values of Young's moduli of PVOH coatings measured by conventional methods (Table 3). While in this work, a Young's modulus (completely independent of coating thickness) of 1.6 ± 0.1 GPa was

determined for supported PVOH coatings was in line with that measured by DMA for a free-standing PVOH film (1.2 ± 0.1 GPa), there is a vast amount of discrepancies in the reported Young's moduli of PVOH coatings in the literature. Various measurement techniques have resulted in Young's moduli ranging from as low as 0.9 GPa to as high as 8.8 GPa [36,37,46,38–45]. The significant variation between these techniques highlights the necessity for studies, such as that presented here, in which a technique is rigorously scrutinized for its precision and adaptability (e.g., to thicker coatings). Also highlighted in Table 3 is the significant lack of available literature on the analysis of supported polymeric coatings – here, less than one third of available data are based on measurements carried out on supported coatings.

Table 3. Comparison of the Young's modulus of PVOH films and coatings as measured using multiple measurements methods on both supported and free-standing samples.

	Measurement method	Young's Modulus GPa	Freestanding or supported?
Buckling measurements	SIEBIMM*	1.6 ± 0.1	Supported
Force measurements	DMA*	1.2 ± 0.3	Freestanding
	DMA [37]	3.8	
	Instron [38]	2.3	
	Instron [40]	2.2	
	Microforce testing machine [43]	4.2	
Indentation measurements	Nanoindentation [36]	1.2	Supported
	Triboscope indentation [47]	3	
	Nanoindentation [48]	2.8	
	TriboIndenter <i>in-situ</i> nanomechanical test system [45]	8.8	
	Atomic force microscopy nanoindentation [46]	2.2	
Tensile test measurements	Stress-strain measurements [42]	0.9	Freestanding
	Universal testing machine [39]	4.2	
	Tensile tester [44]	2.1	
	Universal testing machine [46]	1.3	

*As measured in this work

As with any technique, the limitations of the SIEBIMM method must be understood in order to attain accurate information. It is important to note that small thickness variations induced significant fluctuations in the calculated Young's moduli, which suffer from the heterogeneities of thicker coatings. Consequently, a couple of important factors must be considered: first, the coating thickness and the buckling wavelength should be measured on the same spot on the sample, and secondly, it is recommended to carry out buckling experiments using a minimum of three coating thicknesses such that a linear regression analysis of the data can be performed to minimize the error. It is worth noting that given the availability of equipment such as a spin coater or bar coater, homogeneously thick coatings are relatively easy to prepare, however, demonstrated here is a method (solvent casting) which negates the necessity of specialty equipment (besides that required to measure coating thickness) or an expert skill set which could easily be implemented in an industrial setting to provide high throughput quality control. The adaptability of this method to thicker films in this model system is highly advantageous as it provides a fast and easy method to characterize the mechanical properties of polymer coatings. Additionally, the information provided here will allow us to expand our focus to bio-nanocomposite coatings in which plant-based nanoparticles can be used to reinforce hydrophilic polymer coatings, such as PVOH.

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ABBREVIATIONS

PVOH, polyvinyl alcohol; SIEBIMM, strain-induced elastic buckling instability for mechanical measurement

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SIEBIMM Method for Young's modulus

1D Compression

5 %

