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Mechanical Insights Into Polymeric Multilayers Films Using Nanoindentation and the Structural Compliance Method

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ABSTRACT

This study introduces a novel approach to characterising the mechanical properties of polymeric multilayer films used in photovoltaic (PV) backsheets through nanoindentation (NI). While traditional methods, like tensile testing, measure overall mechanical performance, NI enables layer-specific analysis, which is essential for understanding multilayer structures. Here, we employ the structural compliance correction method to address challenges of specimen-scale flexing and edge effects in NI, enabling accurate measurements of hardness and elastic modulus across distinct film layers. Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and Raman spectroscopy were used to identify the different film layers, which included polyamide (PA), polyvinyl fluoride (PVF), polyethylene terephthalate (PET) and an aromatic polyester-based urethane adhesive. The NI results reveal substantial variation in mechanical properties across layers, with PET showing the highest hardness (200–250 MPa) and modulus values (4–5 GPa). PA offered a hardness of 100–150 MPa and a modulus of 2–3 GPa, followed by PVF with 50–100 MPa hardness and 1–2 GPa modulus. The adhesive layer had the lowest hardness (1.2–1.4 MPa) and modulus (200–400 MPa). Importantly, the structural compliance correction reduced measurement errors caused by specimen-scale flexing and edge effects. Additionally, we observed a small indentation size effect in PET and the adhesive. This study highlights the importance of the structural compliance correction in NI of multilayer films and paves the way for more precise degradation mapping and longevity predictions in polymeric film applications.

1 | Introduction

In some applications involving polymeric films, a single polymer may not fulfill all necessary specifications, making multilayer films essential. Multilayer films are classified into two types: laminated and co-extruded films. Co-extruded films are created by simultaneously extruding and fusing multiple polymer layers, producing a unified structure with superior bonding and barrier characteristics. This approach is ideal for manufacturing flexible, uniform packaging without using adhesives. In contrast, laminated films are composed of separate layers that are bonded with adhesives, typically resulting in greater stability and rigidity [1].

For example, backsheets in photovoltaic (PV) applications—here examined as multilayer structures—are produced through lamination with pressure-sensitive adhesives, where they must meet standards for mechanical stability and electrical insulation [2, 3].

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Typically, these multilayer films consist of three or more layers, each designed to contribute specific, essential properties. The outer layers are formulated to resist environmental factors such as moisture and high temperatures, commonly using materials like polyvinyl fluoride (PVF), polyvinylidene fluoride (PVDF) or polyethylene terephthalate (PET). Historically, materials such as polyamide (PA) and various other fluoropolymers have also been employed [4, 5]. Additionally, an inner adhesive layer or functionalized surface is often incorporated to ensure strong bonding with the PV module's encapsulant. The core layer's primary role is to provide mechanical stability, which is crucial for the durability of PV modules, with PET being the most widely used polymer for this purpose [6].

Currently, the mechanical properties of multilayer films are predominantly assessed through tensile tests [7] but also through more demanding dynamic mechanical analysis (DMA), which is shown in [8] on the example of loudspeaker diaphragms laminated with pressure-sensitive adhesive. Both methods, tensile tests and DMA, yield comprehensive measurements of the entire film. However, recent efforts have been made to use nanoindentation (NI) to characterize multilayer structures and obtain more localized mechanical information. For instance, a multilayer thin film polymer was analysed in a study [9] where individual specimens of each layer were created and measured to determine their elastic moduli by NI. Other NI studies [10–13] involved embedding a multilayer film in epoxy resin to rigidly support the film, while cross-section surfaces were prepared by grinding and then tested.

Despite these advances, a significant challenge remains in investigating the mechanical properties of individual films within multilayer structures in cross-section. The conventional methods of embedding and grinding samples may introduce uncertainties regarding how the surrounding embedding materials, such as epoxy resin, and the grinding process may impact the multilayer structure both chemically, due to the epoxy or the polishing paste, and mechanically, due to the pressure used in the grinding and polishing process [14, 15]. And even if cross-sections are not affected by the embedding or grinding process, the proximity of nearby layers with different mechanical properties can cause edge effects that introduce uncertainties in NI measurements. This study aims to introduce a novel method for characterising the mechanical properties of polymeric multilayer film cross-sections without the need for embedding or grinding and that minimizes errors caused by edge effects.

Jakes et al. developed a NI technique to investigate unembedded wood cells in cross-section by preparing ultra-smooth surfaces using diamond knives and applying the structural compliance (C_s) method to account for specimen-scale flexing and edge effects in the NI analysis [16, 17]. The structural composition of wood cell walls shares similarities with multilayer films, as both consist of multiple viscoelastic solid polymer films with thicknesses in the micrometre range. The structural compliance method is based on the discovery that, to a close approximation, both edge effects in the cross sections of multilayer systems and specimen-scale flexing introduce an inherent C_s into the measurement. The C_s is independent of indentation size, akin to machine compliance (C_m), and contributes to the total measured compliance. Therefore, methods used to measure C_m , such as the Stone-Yoder-Sproul (SYS) correlation [18], were found to be adaptable to also measure C_s .

NI was originally designed to assess hard, rigid and homogeneous materials like metals and ceramics. The Oliver and Pharr (O&P) method [19, 20] is employed in this context to determine the elastic modulus (E_s) by analysing the load–displacement curve, under the assumption that deformation is followed by elastic recovery. In both wood cell walls and polymeric multilayers, the relaxation behaviour is time-dependent and therefore viscoelastic, complicating the interpretation of NI O&P data. Nevertheless, comparisons of viscoelastic NI data from creep tests with O&P data on thermoplastic PMMA have shown that, with a carefully designed experimental setup, viscoelastic modulus from creep tests can be compared with E_s from O&P methods [21].

The representative strain of a Berkovich indenter tip is approximately 8% [22], which lies within the transition zone between viscoelastic and viscoplastic deformation of polymers, adding complexity to the modulus data interpretation. Simpler indenter geometries, such as spherical indenters, may offer clearer insights into polymer NI data, as they operate below the elastic strain limit [21, 23]. However, the choice of a Berkovich indenter in this work is justified by two key factors: it allows for probing small volumes necessary for thin layers and provides a self-similar geometry essential for applying the C_s method to correct for specimen-scale flexing and edge effects [17, 24]. Progress comparing Berkovich NI data with traditional mechanical tests in polymers has also improved confidence in Berkovich NI results in structural polymers like those tested here [25–28]. Recent results demonstrate that Berkovich hardness (H) in structural polymers is directly related to the uniaxial compression flow stress of the polymer at about 8% strain [29]. Furthermore, although viscoelastic moduli assessed with Berkovich NI are typically higher than those recorded by conventional measurements, they follow the same trends with frequency [29]. Collectively, these results demonstrate that Berkovich NI can be used to probe microphysical processes affecting mechanical properties in polymers, similar to how conventional measurements are used to study bulk specimens. The major advantage of NI is that microscale features, such as the individual layers in a multilayer cross-section, can be probed.

The primary objective of this study is to demonstrate the applicability of the C_s method in isolating and correcting for C_s effects in NI measurements of polymeric multilayer material cross-sections that are not embedded. This will enable the acquisition of position-independent results for H and E_s within each layer of multilayer films, which is essential for advancing their development and predicting their service life.

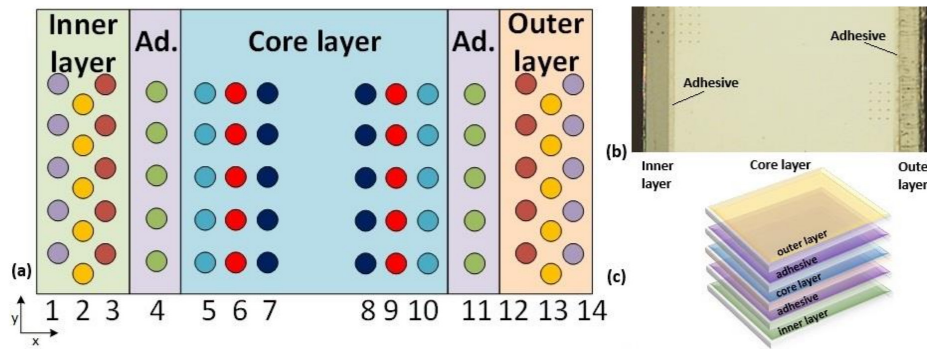


FIGURE 1 | Schematic multilayer in cross-section (a), optical image of the multilayer (b) and multilayer as stack (c) with the layers outer layer (yellow, column numbers 12–14), adhesive (Ad.) (violet, column numbers 4 and 11), core layer (blue, column numbers 5–10) and inner layer (green, column number 1–3). The column numbers in (a) represent different NI locations, and the dots symbolize indentation imprints. For every column number (x-axis), five multicycle indentations were performed in the y-axis to get a statistic for every column in the x-axis. Here, averaged values for each multicycle indent were used to further calculate the average and standard deviation of the five indents in the y direction.

2 | Materials and Methods

2.1 | Multilayer Film Composition

In this study, multilayers from PV applications (backsheets) are investigated. Typically, a PV backsheet consists of a multilayered structure made from various materials (Figure 1). The most common backsheet designs are composed of the following layers: outer layer, adhesive layer, core layer, adhesive layer and inner layer.

The composition of the backsheet tested here was not known. To determine the layer composition, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and Raman spectroscopy were carried out.

2.1.1 | Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FT-IR) spectroscopy measurements were performed to investigate the chemical composition of the multilayer. Both sides of the film were measured using a SpectrumTwo (PerkinElmer Inc., USA) in attenuated total reflectance (ATR) mode using a Quest ATR unit (Specac Ltd., UK) equipped with a diamond crystal. The spectra were recorded over a range from 4000 to 650 cm^{-1} , averaging four scans with a resolution of 4 cm^{-1} .

2.1.2 | Differential Scanning Calorimetry (DSC)

DSC was carried out with a Perkin Elmer DSC 4000 (Waltham, USA) to explore the thermal behaviour of the multilayer in the temperature range of 23 $^{\circ}\text{C}$ –280 $^{\circ}\text{C}$ with a heating rate of 10 K/min. Here, 6.7 mg of the sample was cut and put in a 50 μL pan with a perforated lid. Measurements were carried out in a nitrogen atmosphere to prevent oxidation processes. Enthalpies and peak temperatures for melting and crystallization were evaluated according to ISO 11357-3 [30].

2.1.3 | Raman Spectroscopy

In order to investigate the adhesive between the layers of the film, Raman spectroscopy was applied to the cross-section of the embedded multilayer film [31]. The Raman spectra were measured on a confocal Raman spectrometer of the type LabRAM HR800 (Horiba Jobin Yvon GmbH, Germany) using a green laser with a wavelength of 514.5 nm. An objective with a magnification of 100 was used together with a diffraction grating with 1800 grooves/mm, a hole size of 500 μm and a slit size of 300 μm . The spectra were scanned in the range from 250 to 3800 cm^{-1} with an exposure time of 2 s. Filters were used to avoid burning the sample.

2.2 | Nanoindentation Sample Preparation

To minimize mechanical damage to the samples and chemical changes due to the epoxy or the polishing paste, traditional embedding and grinding methods were avoided in this NI study. Instead, samples were prepared using a precision diamond knife cutting method to produce smooth, unembedded cross-sections based on earlier work by Jakes et al. [24].

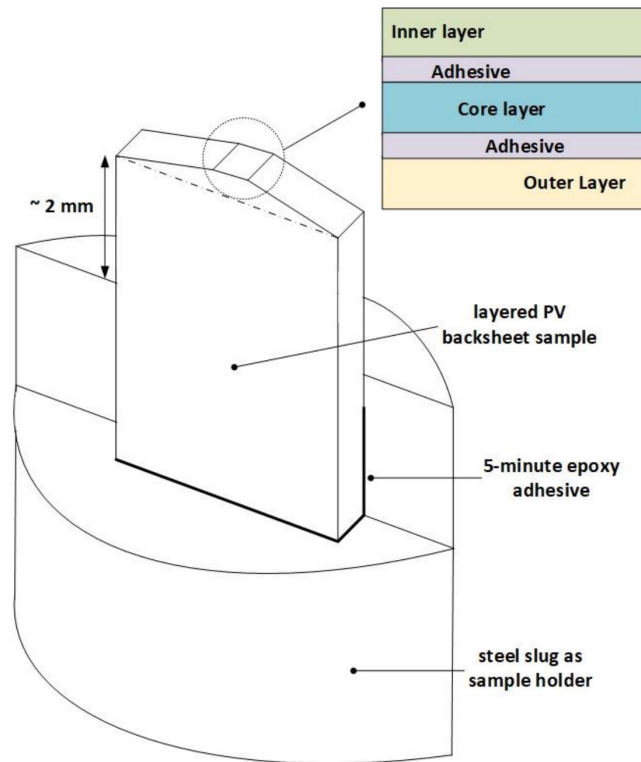


FIGURE 2 | Sample preparation of the layered PV backsheet sample, following [32].

A visibly undamaged 1×1 cm sample of the multilayer was selected for analysis and attached to a steel slug sample holder using a 5-min epoxy adhesive (Figure 2). The sample holder was then fit into a Leica EM UC7 ultramicrotome (Wetzlar, Germany) equipped with a diamond knife. An initial 15° apex was created using a hand razor. Subsequently, the apex was trimmed with the diamond knife, using progressively thinner sections ranging from $2 \mu\text{m}$ down to 200 nm until an ultra-smooth flat surface of adequate size was prepared for NI.

2.3 | Nanoindentation Setup

NI was conducted using a Bruker-Hysitron TI 950 TriboIndenter equipped with a Berkovich diamond tip. Experiments were performed at room temperature measured to be 21°C during the experiments. The relative humidity inside the NI enclosure during the experiments was maintained at 60% using an InstruQuest (Coconut Creek, Florida, USA) HumiSys HF RH generator. Specimens were conditioned in the enclosure for 48 h prior to testing. The C_m , probe area function and tip roundness effects were determined from a series of 80 indentations in a fused silica standard using the load function and the procedures in [16, 18]. Following the calibration reporting procedure prescribed in [16]: Values for the square root of the Joslin–Oliver parameter of $1.190 \pm 0.002 \mu\text{m}/\text{N}^{1/2}$, E_s of $72.0 \pm 0.1 \text{ GPa}$ and Meyer's H of $8.73 \pm 0.03 \text{ GPa}$ (uncertainties are standard errors) were assessed for fused silica calibration indentations with contact depths between 37 and 183 nm; no systematic variations of C_m or Joslin–Oliver parameter were observed in the systematic SYS plot analysis over this range of contact depths.

Multicycle indentation tests were performed in each layer of the film's cross-section to assess properties as a function of indentation size at each NI location shown schematically in Figure 1. For the stiffer layers (inner layer, core layer, outer layer), the load profile in Figure 3a with nine cycles and a final maximum load of 1 mN was used. This load profile is fully described in [33] and was designed to minimize time-scale effects in the measurement of size-dependent properties in viscoelastic materials like polymers. This is achieved by maintaining consistent times for each type of segment for all cycles. In brief, each cycle consisted of an effective 2 s load, 5 s hold at the maximum cycle load, 1.4 s partial unload to 30% of the previous cycle's maximum load and 1 s hold at the partial unload. The final partial unload hold was held for 60 s to measure displacement drift. While the first load time was 2 s, the subsequent eight load times were less and called "effective" because they would have been 2 s if they started at zero load instead of the partial unload load. The adhesive layer was tested using the five-cycle load profile in Figure 3b, which had a final maximum load of only 0.01 mN. The smaller maximum load for the adhesive was necessary to decrease penetration depth and to ensure that the entire indentation impression was within the adhesive layer. The segment times were the same, except for a 0.3 s partial unload time. A shorter 0.3 s unload time was needed to minimize forward creep during the unloading segment in the soft adhesive layer and was determined through an analysis of preliminary experiments with varying unloading times [29]. Only the five larger cycles were used. With a 0.01 mN final maximum load, the loads in the smaller cycles were found not to be reliable because they were near the lower load capabilities of the NI transducer.

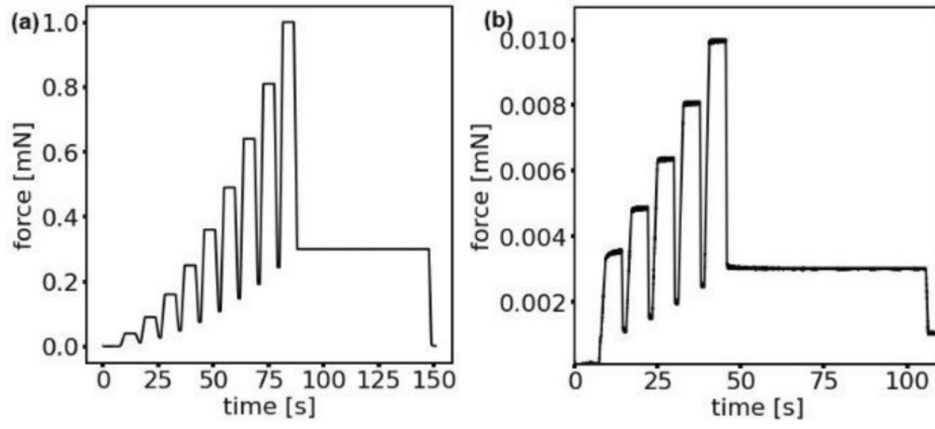


FIGURE 3 | Load profile for measurements on the stiffer layers: outer layer, core layer and inner layer (a), and for the softer adhesive (b): The scale of the load profile is different due to huge load differences.

All indentations were preceded by a lift-off, offset and re-approach to an undeformed surface area to minimize surface detection errors. As shown schematically in Figure 1a, NI was then conducted at five different positions along the y -axis to calculate the mean and standard deviation for each position on the x -axis (index). Displacement drift was determined by fitting the last 30 s of the depth-time trace to a straight line. The slope of this line represents the displacement rate. The entire depth-time profile was then adjusted using the calculated displacement drift rate [33].

The Bruker-Hysitron TI 950 TriboIndenter was also used to perform scanning probe microscopy (SPM) imaging using the Berkovich probe before and after indentation. Z -height square scans $20\mu\text{m}$ or $40\mu\text{m}$ across were obtained in contact mode using a scan rate of 1 Hz and a $1\mu\text{N}$ load setpoint.

2.4 | Modulus Calculation

The E_s and Meyers H were calculated using the O&P method [20], with corrections applied for both C_m and C_s . The results were compared with values not corrected for C_s to highlight the influence of the C_s corrections on the mechanical properties.

The loading, holding at maximum load and unloading segments of NI are predefined in a force and time loading function (Figure 3), while the indentation depth is recorded accordingly. Meyers H is defined as follows:

$$H = \frac{F_{\max}}{A_0} \quad (1)$$

with the maximum force $F_{\max}$ and the contact area A_0 . A_0 is calculated using the area calibration function of the Berkovich probe, which is expressed as a function of the indentation contact depth h_c , such that $A_0 = f(h_c)$ [34]. Here, h_c is defined by $h_{\max}$, the indentation depth at $F_{\max}$ and the contact stiffness S as follows:

$$h_c = h_{\max} - 0.75 \frac{F_{\max}}{S} \quad (2)$$

The elastic properties are calculated by fitting the unloading curve of the load (F)–penetration (h) curve to the following:

$$F = \kappa (h - h_f)^m \quad (3)$$

where κ , h_f and m are fitting parameters [20]. The S at the beginning of the unloading curve is then calculated by differentiating F and substituting $h_{\max}$ for h .

$$S = \frac{dF}{dh} = m\kappa (h_{\max} - h_f)^{m-1} \quad (4)$$

It is assumed that the unloading segment represents (visco-)elastic deformation, in contrast to the loading and holding segments, which exhibit (visco-)elastic and (visco-)plastic behaviour. Additionally, it is presumed that some unavoidable plasticity occurs at the beginning of the unloading curve; therefore, the fitting of the unloading curve to Equation (3) is typically performed excluding the first 5% of the unloading data. In this work, Equation (3) was fit from 40% to 95% of $F_{\max}$ of each unloading slope. Subsequently, the elastic properties are calculated using the contact compliance C_p , which is the inverse of S :

$$C_p = \frac{1}{S} = \frac{1}{E_{\text{eff}} A_0^{1/2}} \quad (5)$$

with the effective modulus of contact E_{eff} . The Young's modulus E_s can then be calculated

$$\frac{1}{E_{\text{eff}}} = \frac{\pi^{1/2}}{2\beta} \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_d^2}{E_d} \right) \quad (6)$$

where E_d is the elastic modulus of the diamond tip (1137 GPa), ν_d is the Poisson's ratio of the diamond (0.07), ν_s is the Poisson's ratio of the sample and β is a correction factor. Poisson's ratio of a multilayer on the microscale is highly dependent on its production process. Here, the multilayer is produced through lamination of the single sheets with pressure-sensitive adhesives. The single sheets themselves are produced by an extrusion followed by biaxial stretching in most cases. This leads to the assumption that the Poisson's ratio on the cross-sectional multilayer is location-dependent. Therefore, a location-dependent Poisson's ratio would likely lead to more accurate E_s results. Due to a lack of literature on such a value, it was decided to use a constant value. In this study, ν_s was assumed to be 0.35 for all polymer films, as is typical for hard thermoplastics [35]. In this study, the numerical factor β was assumed to be one, although there is some debate regarding its value [36].

2.5 | Structural Compliance Analysis

The basic description of NI relies on testing a homogeneous sample, which is treated as a rigidly supported half-space. However, for non-embedded multilayer samples, this assumption of rigid support cannot be made, as the sample may flex when the indenter tip is pressed into it. The C_s can also arise when indents are placed near free edges or interfaces between neighbouring layers that have different properties. Not accounting for the C_s for indents near free edges or near a more compliant layer will lead to an overestimation of the indentation depth, and consequently, an underestimation of the E_s . Conversely, conducting NI adjacent to a stiffer layer would result in an underestimation of the indentation depth and an overestimation of E_s . As a further consequence, unaccounted-for C_s will also introduce an error in the H measurement.

Jakes et al. developed a method to correct load-depth traces for specimen-scale flexing and edge effects [17, 24, 37]. Although initially designed for investigating wood cell walls, this method is applied here to polymeric multilayer films. They introduced C_s to account for edge effects when indentations are near a free edge or a heterophase layer interface. C_s is independent of the NI size and contributes to the total compliance (C_t) alongside the C_m . The property C_m is a constant machine characteristic that can be calculated during a calibration process and removed from the data prior to analysis [16]. In contrast, C_s is highly location-dependent and must be measured for each individual indentation. In this study, quasi-static NI is employed using multicycle indentation tests to obtain C_t as a function of F_{max} . Then, the modified SYS equation is used (assuming data are already corrected for C_m prior to analysis) [18]:

$$C_t F_{\text{max}}^{1/2} = C_s F_{\text{max}}^{1/2} + J_0^{1/2} \quad (7)$$

where $J_0^{1/2} = H^{1/2} E_{\text{eff}}$ is the square root of the Joslin–Oliver parameter [19]. Now, $C_t F_{\text{max}}^{1/2}$ is plotted against $F_{\text{max}}^{1/2}$, resulting in a straight line with a slope equal to C_s when H and effective modulus (E_{eff}) are assumed to be independent of the indentation size. C_s can now be utilized to correct the load-depth trace in the same manner as the C_m correction is applied. The corrected values of H and effective modulus (E_s) can then be calculated from the corrected load-depth trace as described earlier.

3 | Results and Discussion

3.1 | Layer Chemical Characterization

FTIR-ATR spectra of the inner layer show pronounced PA peaks according to Figure 4a, whereas spectra of the outer layer show peaks of PVF according to Figure 4b [38]. The middle layer and adhesive of the multilayer could not be detected using FTIR-ATR. Therefore, additional DSC measurements were conducted, resulting in endothermic melting peaks at 176°C, 192°C and 254°C, which are typical peaks for PA12, PVF and PET (polyethylene terephthalate), respectively (Figure 5) [4, 5, 39].

To further characterize the thin adhesive layer, which could not be identified by FTIR and DSC, Raman spectroscopy was employed. Figure 6 presents the Raman spectrum of the adhesive, revealing that it consists of an aromatic polyester-based urethane after [31, 40–42] with the respective measurement position.

Collectively, the chemical analyses identified the inner layer as polyamide (PA), the outer layer as polyvinyl fluoride (PVF) and the core layer as PET. And an aromatic polyester-based urethane was identified as the adhesive bonding the layers together.

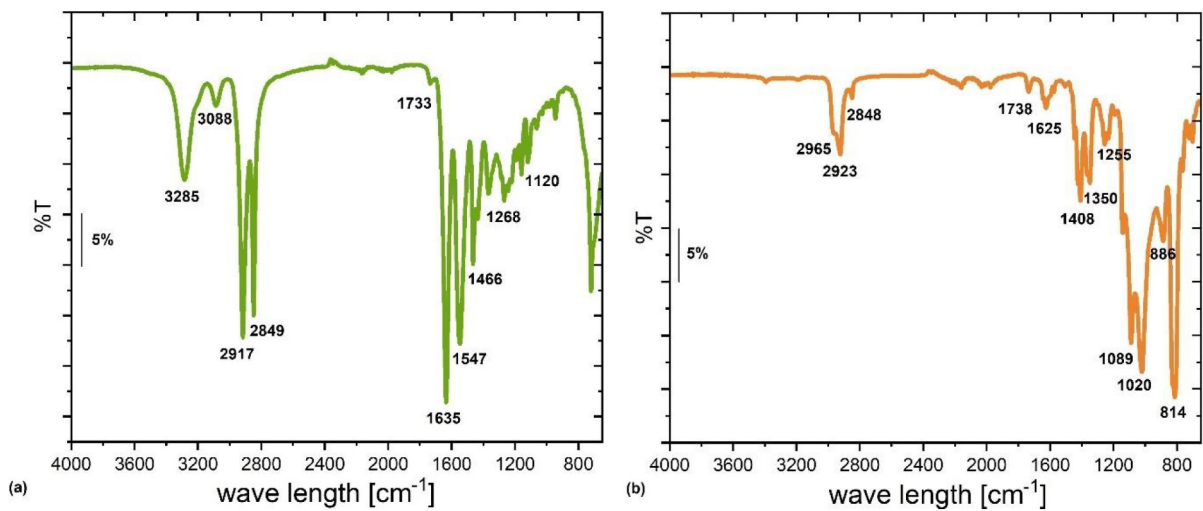


FIGURE 4 | FTIR-ATR spectra from the inner layer (a) and the outer layer (b): The inner layer shows significant PA peaks, and the outer layer shows PVF peaks as well as PA peaks.

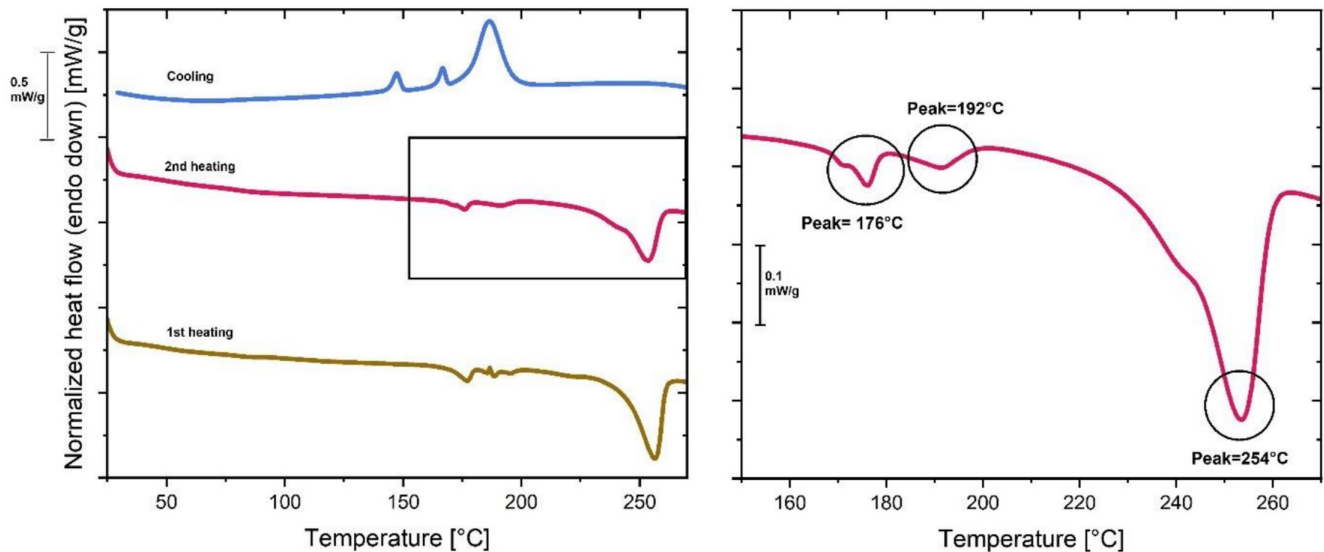


FIGURE 5 | DSC results of the multilayer with melting points at 176°C, 192°C and 254°C, which are typical peaks for PA12, PVF and PET, respectively.

3.2 | Layer Mechanical Characterization Using NI

Multicycle indentations were placed in each of the five layers of the multilayer cross-section that was prepared using a diamond knife without any embedment. Figure 7 shows optical microscopy and SPM images of the prepared surface with the indentations. All the prepared layer surfaces were found suitable for NI with readily observable indent impressions in the SPM images obtained after the experiments. The PA, PET and adhesive layers were smoother than the outer PVF layer on the right side of the film. In both the optical and SPM images of the PVF layer, there appear to be microcracks present. In the optical image, the PVF layer microcracks can be observed as darker lines mostly oriented horizontally. The crack indicated by the black and white arrow in Figure 7a is also shown in the SPM image in Figure 7f, where a discontinuity in height is observed, which further supports the assumption that the features are microcracks. It remains unknown if the microcracks were initially present in the sample or if they were caused by the sample preparation. Moffett [43] et al. show that material aging causes the multilayer backsheets to crack. The storage time of the multilayer sample in our laboratories is unknown, so natural aging and, furthermore, cracking of the backsheets could also be a reason for the PVF cracks. Presumably, these cracks would weaken the strength and lower the overall stiffness of the material backsheet as a structural component, even if the intrinsic properties of the material did not change or even increased. Fortunately, as shown later in this section, the effects of the microcracks on the NI measurements can also be minimized using the C_s method. During surface preparation, the cutting direction was parallel to the layer long axes, which is the vertical direction in Figure 7. Imperfections in the diamond knife edge caused some vertical knife marks, such as indicated with the white arrows in Figure 7. Comparison of experiments on and

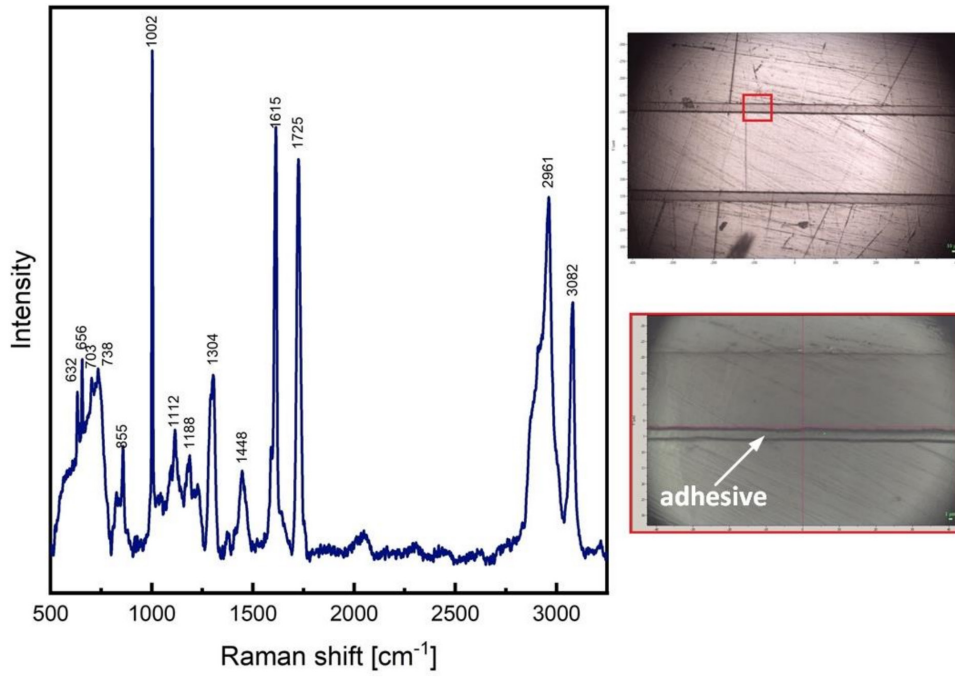


FIGURE 6 | Raman spectrum of the adhesive with the respective measurement position.

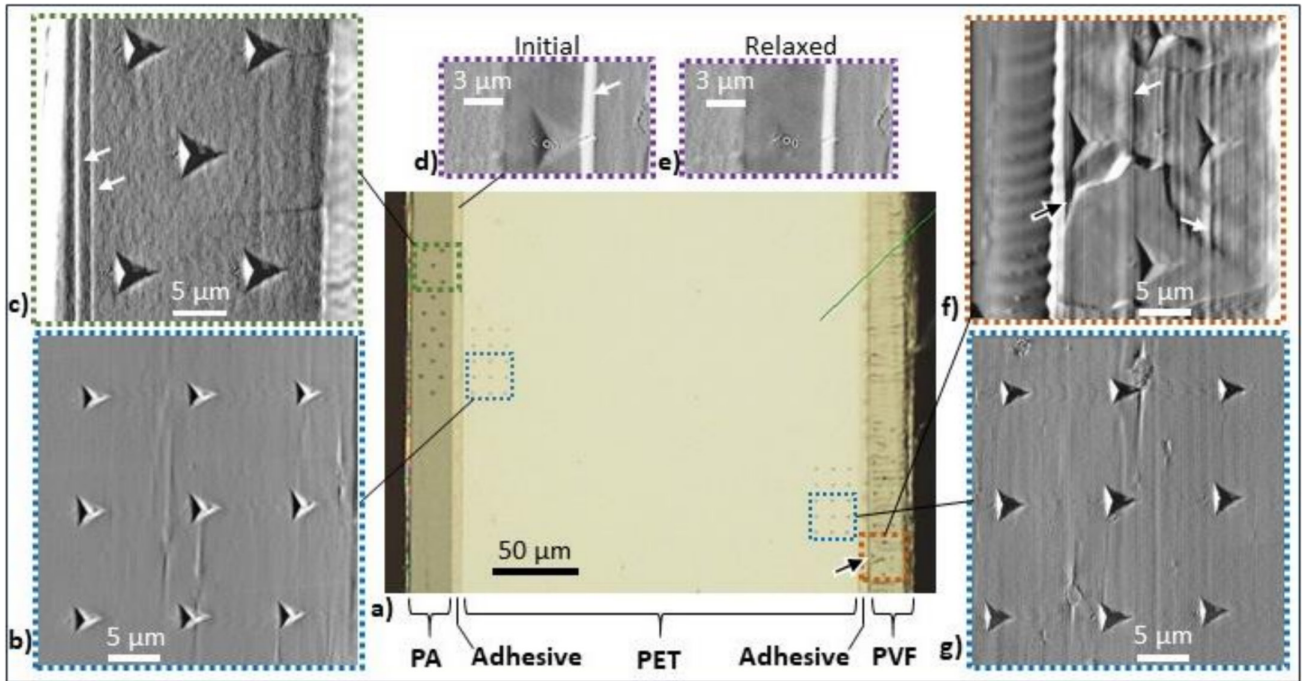


FIGURE 7 | Optical (a) and SPM (b–g) images after indentation of the cross-sectional multilayer film. SPM images are slope shaded to better visualize the surface features. For the adhesive, the initial SPM image (d) was obtained about 3 min after the experiment, and the relaxed SPM image (e) was obtained about 10 min after the experiment. White arrows indicate examples of knife marks, which appear as vertical lines in the SPM images. The black and white arrows in (a) and (f) indicate an example of the same crack in the PVF layer observed in optical and SPM images, respectively.

away from knife marks revealed that these knife marks had minimal influence on the NI measurements. Therefore, indentations overlapping the knife marks were included in the analysis.

In Figure 8a,b, the H and E_s for the PET, PA and PVF layers are given for all nine indentation cycles from Figure 3a before correcting for the C_s . The data in Figure 8 are corrected for C_m . For PET, the H for the two smallest indents decreases noticeably with decreasing indentation size. This trend of decreasing H for the smallest PET indents is not consistent with the expected effect of an unaccounted-for C_s . C_s effects diminish with smaller indent sizes. Additionally, the C_s has a relatively small effect on H as compared with E_s [37].

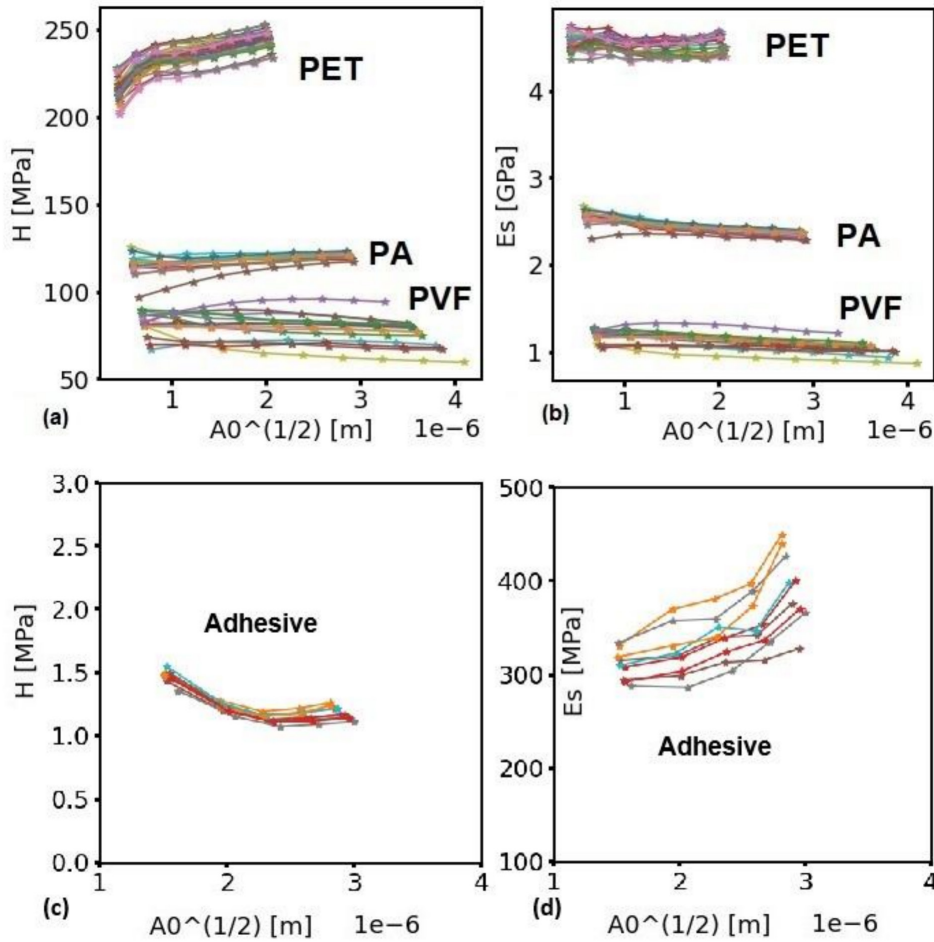


FIGURE 8 | H of PET, PA and PVF (a) E_s of PET, PA and PVF (b) H of adhesive (c) and E_s of adhesive (d) as a function of indentation area for the layers PET, PA, and PVF for the nine (for PET, PA and PVF) and five (for the adhesive) indentation cycles from Figure 3 before correction for the C_s .

This small effect on H is because, in the calculation of h_c used to determine A_0 , an unaccounted-for C_s has opposite effects on the two terms in the right-hand side of Equation (2). For example, while an unaccounted-for positive C_s would cause an overestimation of $h_{\max}$, it would lead to an underestimation of S . The underestimated S increases the value for the second term in the right-hand side of Equation (2), which partially compensates for the larger $h_{\max}$ in the calculation of h_c . The effect of C_s on H is relatively small because the effect on A_0 is small, and $F_{\max}$ does not depend on C_s . In contrast, the C_s effect is larger in E_s because E_s also directly depends on S through Equation (5). The decrease in E_s with increasing size for PA and PVF is consistent with an unaccounted-for positive C_s . Therefore, the H size effect for the smallest PET indents may be real and would violate the assumption of the C_s method that E_s and H are independent of indentation size. There is also noticeably more noise in the smallest two indentations for PA and PVF. We therefore decided for all three materials to remove the first two data points from each measurement in the next step to calculate the C_s , and furthermore, the C_s -corrected E_s and H values. The reason for the uncertainties in the smallest two indents is not fully understood. Surface roughness or oxidation effects may have contributed. For the prepared PET surface, over the span of weeks, some liquid droplets formed and could be observed with optical microscopy. It was also possible that there was some migration of this liquid from the PET surface before the NI experiments that affected the measured near-surface properties.

The adhesive layer's E_s and H from the five indentation cycles in Figure 3b are shown in Figure 8c,d. These data have not been corrected for C_s , but have been corrected for C_m . This layer is much softer than the three stiffer layers, with a measured H about two orders of magnitude lower and an E_s about one order of magnitude lower. The indentation impression in the adhesive (Figure 3d) could also be observed to relax over the span of hours after the experiment (Figure 3e). Such relaxation was not observed in the stiffer materials. The much lower values of the mechanical properties and the faster impression relaxation are characteristic of a soft elastomeric or rubbery material. In NI, such soft materials are often studied with larger spherical probes or punches to increase the loads and contact stiffnesses of the experiments [44]. However, the thinness of the adhesive layer studied here required the use of a sharp indenter, such as a Berkovich probe, to test it. With increasing indentation size, E_s increased, and H decreased. The increase in E_s was consistent with an unaccounted-for negative C_s , which would be expected with testing a soft material near interfaces with much stiffer materials. The size effect in H was not consistent with a C_s effect. It is uncertain whether the size effect was real or related to another measurement artefact caused by surface detection issues or testing a soft material with a Berkovich probe near the lower load limits of the NI transducer. Nevertheless, data from all five indentation cycles were included for the adhesive in the next steps, measuring and correcting for the C_s .

Figure 9 shows the position-dependent C_s values across the BS multilayers, with larger values near the adhesive interfaces (Indices 3, 5, 10 and 12) and near the BS edges (Indices 1 and 14). This behaviour indicates that the adhesive acts as a mechanical free edge, reducing support to the surrounding layers and adding to the effects of specimen flexing. The adhesive layer exhibited negative values compared with the adjacent PA, PET and PVF layers, indicating that the adhesive is much softer than the other layers. The standard deviation of C_s for PVF is greater than that for PET and PA, likely due to imperfections and microcracks observed in the optical and SPM images of PVF (see Figure 7). A microcrack acts like a free edge, so an indentation placed near a microcrack, even at the centre of the film, will exhibit a higher C_s . This increased variability in C_s highlights the importance of evaluating C_s at each indentation location. Additionally, the C_s of the core PET layer is higher near the adhesive layer (Indices 5 and 10) and lower in regions farther from the adhesive (Indices 6–9).

Figure 10 presents the Joslin–Oliver parameter J_0 as a function of the indentation positions for the different layers. J_0 is an area-independent material parameter, defined as $\frac{H}{E_{eff}^2}$. When derived from a SYS plot, J_0 is also independent of C_s . The fact that J_0 remains consistent across positions within each layer suggests that the material properties do not vary through the thickness. The differing J_0 values across the layers indicate that each layer possesses distinct mechanical properties.

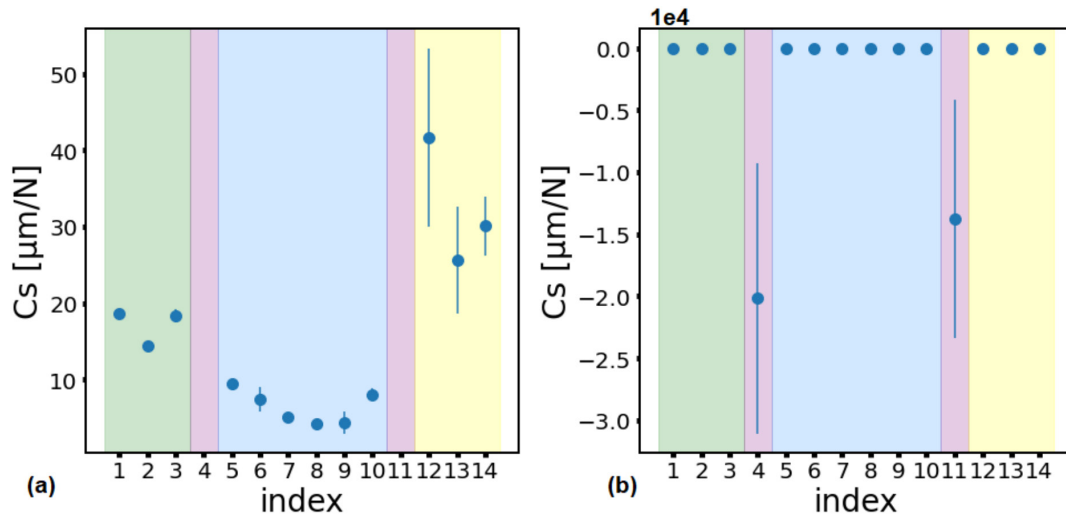


FIGURE 9 | C_s as a function of the index position of the indents for the layers PA (1–3), PET (5–10) and PVF (12–14) (a), C_s as a function of the position for the adhesive (4,11) (b): C_s is presented in terms of the mean with error bars representing the standard deviation from five measurements according to the measurement plan in Figure 1a.

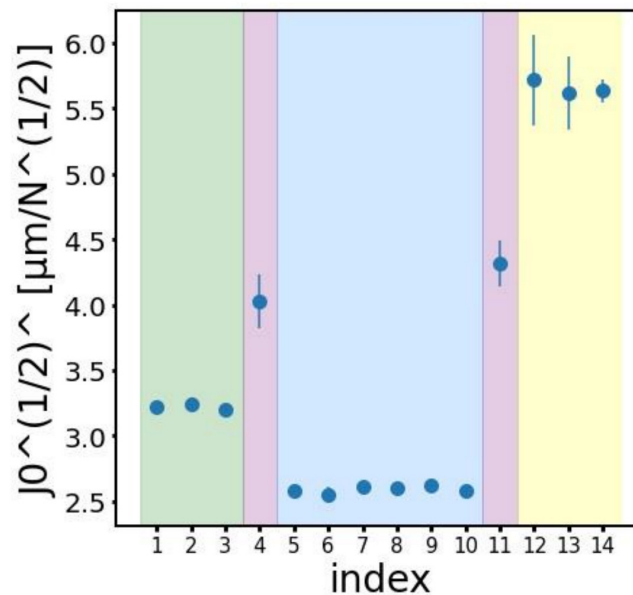


FIGURE 10 | J_0 as a function of the position of the indents for the layers PA (1–3), PET (5–10) and PVF (12–14). J_0 is calculated in terms of mean and standard deviation from five measurements in column (y-axis) (compare Figure 1).

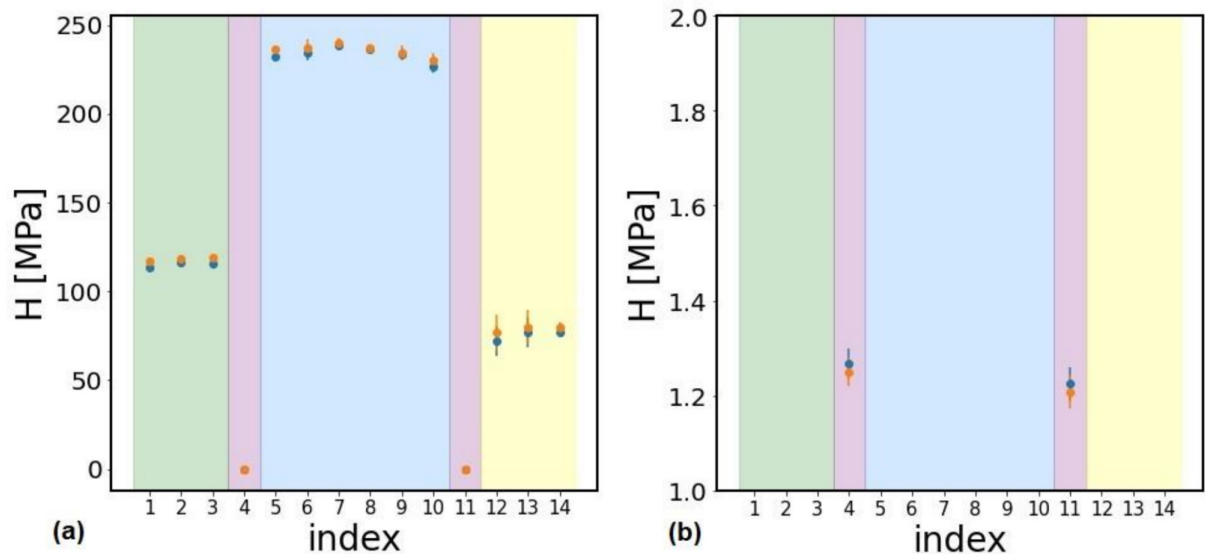


FIGURE 11 | Uncorrected H (blue) and C_s corrected hardness (orange) as a function of the position of the indents for the multilayer (a) and hardness zoom in to the adhesive layer (b): hardness is calculated in terms of mean and standard deviation from five measurements in column (compare Figure 1).

C_s typically has a smaller impact on the H calculation than on the calculation of E_s . This is because C_s has a strong influence on the measured stiffness, from which E_s is calculated, but comparatively little effect on load and area, from which H is determined [37]. Therefore, as shown in Figure 11, only a small difference is expected between the uncorrected (blue) and C_s -corrected (orange) H values. PET, being the core layer, exhibits the highest H in the multilayer structure. The adhesive layer, zoomed in Figure 11b, shows very low H in contrast to the other layers.

Figure 12 shows the uncorrected (blue) and C_s -corrected (orange) E_s values as a function of indent position (index) across the multilayer. The C_s -corrected E_s is significantly higher for the PA (Figure 11b), PET (Figure 12c) and PVF (Figure 12d) layers compared with the uncorrected E_s , confirming that specimen flexing caused an underestimation of E_s . In Figure 11b, the uncorrected PA E_s is lower near the free edge (Index 1) and near the adhesive interface (Index 3), indicating that the adhesive is soft enough to behave like a free edge mechanically. After C_s correction, there is no significant difference in E_s between positions with Indices 1, 2 and 3. A similar pattern is seen in Figure 10c, where the uncorrected PET E_s is lower near the adhesive interface (Indices 5 and 10) and higher in the bulk region (Indices 6–9). In Figure 11d, no significant difference is observed in E_s between the bulk and edge regions of PVF. The uncorrected and the corrected E_s of the adhesive are shown in Figure 10e. Here, the E_s is lower after C_s -correction due to the negative C_s from Figure 8b.

Utilising the C_s method will be invaluable to future durability studies in which degradation will be expected to occur as a gradient across a layer. Because the C_s correction was shown here to remove measurement artefacts caused by edge effects, its utility in future studies should allow actual degradation effects on material properties near edges to be measured more reliably. Additionally, the fact that the adhesive layer behaves like a free edge highlights the necessity of using the C_s method when testing multilayer film cross-sections, even when the specimen is embedded in epoxy to minimize specimen-scale flexing.

In Figure 13, H and E_s are plotted as functions of the indentation size after correction for the C_s . The initial two data points at low indentation depths for the PA, PET and PVF layers were excluded due to surface uncertainties as previously discussed. For the PA and PVF (Figure 13a,b), H and E_s are both now mostly independent of A_0 and therefore also of the indentation depth. The main effect of the C_s correction in PA and PVF was to remove the size effect in their E_s . However, for the PET layer, an indentation size effect (ISE) appears, with H and E_s increasing with larger A_0 . And in the adhesive, an ISE is present with the H and E_s both now decreasing with increasing indentation size.

An improved understanding of the ISE may provide useful information about the deformation mechanisms controlling the mechanical properties. For example, the H ISE in crystalline metals has been interpreted using strain gradient plasticity theories to better understand size-dependent plasticity mechanisms [45]. However, the ISE in polymers is less understood. In literature, the presence of phenyl rings seems to correlate with a stronger ISE in polymers [46]. Also, for some crystalline polymers, size effects are sometimes attributed to morphology such as crystalline subphases [23]. Another complicating factor in studying the ISE in these thin film layers is that an ISE would cause a minor artefact in the C_s analysis because an ISE violates the assumption of the C_s method that H and E_s are independent of size. A H ISE in which H increases with increasing size, like in PET, would lead to a slight overestimation in the calculation of C_s . In PET, this likely contributes to the E_s size dependence observed in Figure 13b. Conversely, if H decreases with increasing size, it will cause an underestimation of C_s . This would lead to a decreasing E_s , like observed for the adhesive in Figure 13d.

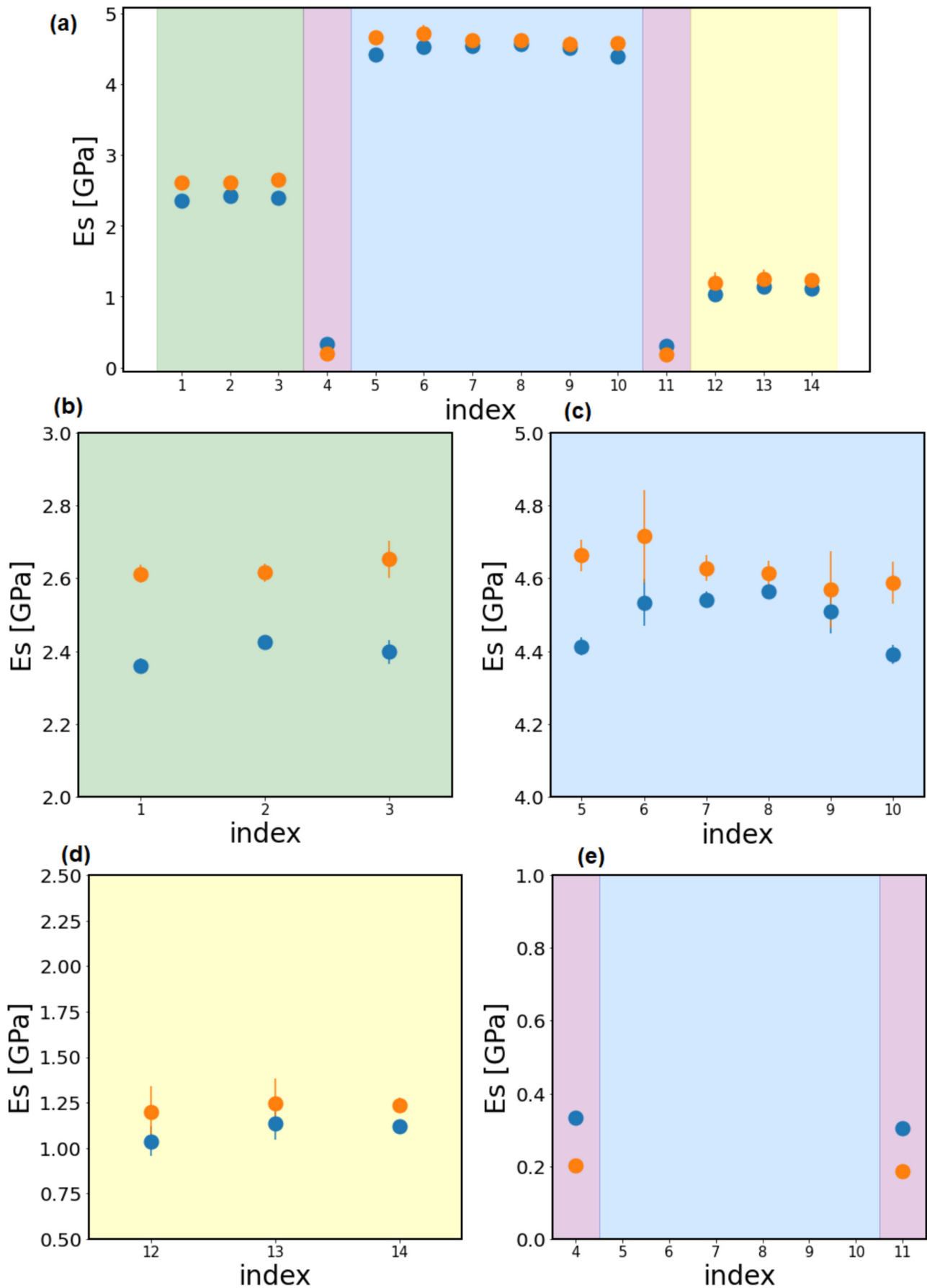


FIGURE 12 | Uncorrected E_s (blue) and C_s corrected E_s (orange) as a function of the position on the multilayer (a), as zoom in for PA (b), PET (c), PVF (d) and the adhesive (e): E_s is calculated in terms of mean and standard deviation from five measurements in column (y-axis) (compare Figure 1).

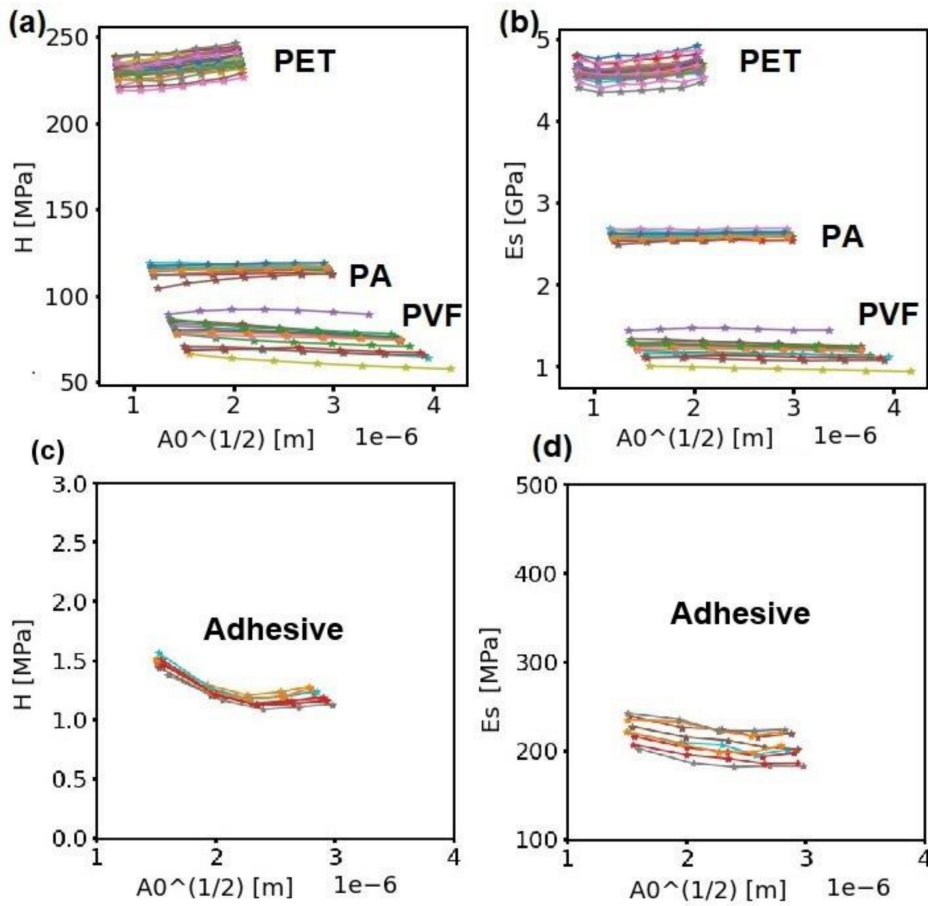


FIGURE 13 | H (a) and E_s (b) as a function of indentation area for the layers PET, PA and PVF and H (c) and E_s (d) as a function of indentation area for the adhesive after correction for C_s .

Furthermore, surface detection issues, especially in very soft materials like the adhesive, could cause incorrect depth measurements that lead to incorrect contact depths and contact areas. A systematic error in surface detection would cause an ISE to appear in both H and E_s .

A strategy to help overcome these challenges with C_s and surface detection uncertainties would be to conduct a more thorough analysis in which contact areas are measured directly from high-resolution images of residual indent impressions [27–29]. Contact areas measured from images are independent of any uncertainty in C_s or surface detection. Therefore, any H ISE could be directly studied. And E_s could be calculated without the potential systematic errors caused by surface detection issues. Future research that includes precise measurements of residual contact areas using high-resolution imaging techniques would be valuable for gaining a deeper understanding of the ISE in PET and the adhesive.

4 | Conclusion

In this study, the structural composition and mechanical properties of laminated multilayer films were investigated using FTIR, DSC, Raman spectroscopy and NI. The chemical analyses revealed the composition of the multilayers as polyamide (PA), polyethylene terephthalate (PET) and polyvinyl fluoride (PVF) for the inner, core and outer layers, respectively. The layers were found to be bonded together with an aromatic polyester-based urethane adhesive. For NI, ultra-smooth surfaces were prepared using a diamond knife without embedment to avoid potential artefacts caused by embedding materials or grinding. NI measurements revealed differences in E_s and H for the different layers, with PET exhibiting the highest values and the adhesive showing the lowest. Importantly, the C_s correction was vital in reducing measurement errors arising from specimen-scale flexing and heterophase interfaces or free edges near the indents. Without the C_s correction, E_s values within a layer were observed to depend on proximity to nearby free edges or interfaces between layers. While E_s for PA and PVF decreased as a function of indentation size, the adhesive layer showed a concomitant increase in both H and E_s under the same conditions. After applying the C_s correction to account for specimen-scale flexing and edge effects, properties were found to no longer depend on proximity to edges or interfaces, and there was no size effect in PA or PVF. Size effects were still observed in PET's and adhesive's H and E_s values after the C_s correction. Additional future work should be undertaken to better understand the size effects in PET and adhesive. Interestingly, the soft adhesive layer was found to be

so compliant that it behaved mechanically like a free edge, which indicated that, even if this multilayer film had been embedded to prevent specimen-scale flexing and free edge effects, the C_s correction would still be needed to accurately measure the properties of the stiff layers near the adhesive. The NI approaches developed here to study multilayer structures, such as PV backsheets, will enable future studies to more accurately map polymer degradation across individual layers and near free edges, where the degradation is likely to be most severe. These improved measurements will facilitate more accurate predictions regarding their service life.

Author Contributions

P. Christoeffl: conceptualization, investigation, writing – original draft, methodology, visualization, writing – review and editing. **J. E. Jakes:** conceptualization, data curation, formal analysis, investigation, methodology, resources, writing – review and editing. **J. Geier:** investigation, validation, writing – review and editing. **G. Pinter:** conceptualization, resources, supervision, writing – review and editing. **G. Oreski:** conceptualization, funding acquisition, supervision, resources, writing – review and editing. **D. Stone:** methodology, conceptualization, supervision, writing – review and editing. **C. Teichert:** supervision, writing – review and editing.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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