Nanoscale topographical characterization of permeability-related features in the production of polymeric films for food packaging

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Abstract. Polymeric films play a vital role in food packaging, offering protective barriers that preserve the quality, safety, and shelf life of food products. Their performance depends on properties such as mechanical strength, thermal stability and permeability. Permeability is particularly important as it regulates the transfer of gases from the environment to food. Thus, permeability affects the shelf life, taste and safety of food products. The interaction between nanoscale surface features and permeability is a critical but under-explored aspect of film design. This study aims to test capability of surface topographical characterization as an alternative quality inspection tool for permeability in commercial polymer films. Advanced techniques such as Atomic Force Microscopy (AFM) are used to characterize surface features including roughness and morphology. The results will provide an alternative route for the permeability quality control in manufacturing processes of state-of-the-art commercial polymer films for food packaging.

Introduction

Food packaging represents a critical processing step in secondary agri-food industry because it severely affects food products quality, with functions that encompass product safety during transport to shelf-life extension. In fact, food products exposition in uncontrolled packaged environments might promote both biochemical and physical alterations in the good, e.g. bacterial metabolism, colour and texture variation, which depending on the case could be harmful to the consumers' health [1]. Therefore, both packaging in modified atmosphere and packaging technologies have been widely studied to extend the shelf-life by preserving organoleptic properties [1], while strict international regulations have been put in place to control requirements of packaging in direct contact with food [2]. In particular, polymeric films for food packaging represent a critical component for ensuring intermediate life-span duration of goods both for industry, distribution, and consumers. Polymeric films offer a protective barrier between food products and external environmental factors, thereby preventing contamination, dehydration, and oxidation. Gas permeation process exerts a substantial influence on the shelf life, organoleptic properties, and safety of packaged foods, emphasizing the necessity for precise control and comprehensive understanding of these properties in the development of effective packaging solutions [3]. The widespread adoption of polymeric films in food packaging applications can be attributed to their versatility, cost-effectiveness and lightweight nature. Polymeric films for food packaging are mostly manufactured by extrusion process, which allows high degree of control over the thickness and composition of the resultant film [4]. The materials most frequently employed in the production of such films include polyethylene (PE), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polypropylene (PP), and polyvinylidene chloride (PVDC), and polyamide (PA) [5]. Commercially, PVC and PVDC have been more attractive than PE recently thanks to their greater barrier and capability of withstanding higher temperature, opening to wider range of packaging atmospheres and applications [6]. Also, more recently, extensive research on high-barrier properties material, e.g. based on multilayer structure [6], bio-based materials [7], and surface functionalized films by ceramics layers [8].

The distinct barrier properties of these materials are tailored to specific requirements for food packaging. The primary function of these films is to act as barriers to oxygen (O_2) and water vapour ($H_2O_{(v)}$), thereby preserving the integrity and freshness of food products. Usually, the barrier properties of these films are quantified using permeability (*P*) measurements, and the gas transmission rate (*TR*), typically of oxygen (*OTR*) and water vapour (*WVTR*), across the film in standard tests conditions [9]. Respectively, the *P* describes the flux per unit area and per unit partial pressure of a certain gas across a certain material; *P* is a thickness (*t*) and pressure independent parameter, it is a material intrinsic property, and is expressed in SI units in $mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$, even though in the practice several other units are used. On the other hand, *TR* is the permeability per unit thickness, i.e. $TR=P/t$, and allows catering for the contribution of the film thickness [3,9,10]. The determination of gas *P* and *TR* of polymeric films for food packaging is governed by a series of regulatory frameworks, including ISO 15105 and ISO 15106 [11,12]. Table 1 reports typical values for the most common food packaging film polymers. These frameworks delineate the methodologies for conducting such measurements. Whilst these standard permeability tests provide reliable data, they are often time-consuming, requiring long stabilization time for the baseline evaluation, which makes them less feasible for rapid quality control assessments in industrial settings. The permeability of a material depends on several factors, e.g., the polymer composition, temperature, humidity, and film morphology. In particular, a positive correlation has been shown in sparse cases between permeability and topography [13,14]. The roughness of a film's surface has been demonstrated impact gas diffusion through films, with smoother surfaces generally exhibiting lower permeability [15]. However, literature only reports root mean square height parameter Sq neglecting other surface parameters which might be suitable for describing a porous structure, e.g., the average height gradient.

Table 1 Reference gas transmission rate value for oxygen (OTR) and water vapour (WVTR) of typical polymeric materials for films for food packaging (LD-PE is low-density PE and HD-PE is high-density PE). Unit *d* is day (86400 s). Values refer to 38 °C and 90% relative humidity [16,17]. Higher permeability corresponds to lower barrier. WVTR is the conventional unit as per ISO 15106 [14].

	LD-PE	**HD-PE**	**PP**	**PET**	**PVC**	**PA**	**PVDC**
OTR / $cm^3 \cdot m^{-2} \cdot d^{-1} \cdot atm^{-1}$	6500-8500	1600-2000	2000-4500	100-150	20-100	50-75	2-4
WVTR / $g \cdot m^{-2} \cdot d^{-1}$	10-20	3-10	5-15	15-20	5-10	500-1000	0.5-1

This work aims at leveraging partial results presented in the literature to test capability of surface topographical characterization as an alternative quality inspection tool for permeability. This would allow much faster and readily usable inspection and quality verification methods than current standard permeability tests, which can take as long as 1 day. To bridge this gap, this work will focus on commercially available films for food packaging to provide suitability of surface topography measurements in assessing quality differences and typical variability of roughness values of commercial food packaging films. In particular, the work will investigate the variability of surface topography parameters for commercial polymeric film for food packaging. Furthermore, the study will investigate representativeness of different measurement length scale by characterizing film both at nano-scale by Atomic Force Microscopy (AFM) and at micro-scale by surface topography optical measuring instrument. Such investigation will provide insight representativeness of characterization, which is typically limited to AFM [15].

Materials and Methods

This work focuses on assessing the variability of surface topography of commercially available customer-grade polymer films for food packaging. Considering the commercial availability of the considered products, legal requirements linked to quality tolerances for permeability are considered satisfied [2].

Thickness measurements were performed replicating three measurements with a Sensofar SNeox Confocal Microscope with a 20× magnification objective (squared pixel of 0.69 µm) [18].

Topographical measurements were performed considering two length scale: micro- and nano-scale. Per each measurement length scale, three measurement replications per condition were performed to increase the degrees of freedom to estimate random errors. Measurements were performed by stretching a sample of polymeric food packaging film over a pair of silicon wafer shards with a gap in between, and measurements were performed on the free area, to eliminate any effect of the substrate. Microscale surface topography was assessed by performing measurement the surface of the film by a Sensofar SNeox Coherence Scanning Interferometer (CSI) equipped with 20× magnification Mirau objective, with 0.40 Numerical Aperture, squared pixel size of 0.69 µm, and field of view (FoV) of (845×707) µm. The instrument was calibrated as per ISO 25178-700:2023 showing a measurement noise of 0.78 nm. Scale limited (SL) surface topography was evaluated by a sequence of a F-operator (levelling by subtraction of least-square fitted plane), robust gaussian S-filter (N_{is} of 2.5 µm), and L-filter (N_{ic} of 0.25 mm) [19,20]. The N_{is} follows a 3:1 ratio with the maximum sampling distance, approximated by the pixel size, and the N_{ic} a 100:1 ratio with the N_{is}, which is the smallest choice according to the standard [19,20]. Nanoscale surface topography was assessed by measuring the surface of the film by an Anton Paar Tosca400 atomic force microscope (AFM) having a measurement noise of 11 pm. Measurements were performed in tapping mode investigating a FoV of (10×10) µm with a lateral resolution of 25 nm. To elicit the comparison of the two measured scales, only levelling was performed [21].

The considered measured and post-processed topographies were characterized in terms of height and hybrid surface topography parameters, namely the arithmetic mean height Sa, the root mean square height Sq, the maximum pit depth Sv, the maximum height Sz, the root mean square gradient Sdq, and the developed interfacial are ratio Sdr [19]. Surface characterization was performed by MountainLab v8.1.

Table 2. Factors, Levels and nesting of the factorial design. “Manufacturer” is nested in “Material”, and “Batch” is nested in “Material” and “Manufacturer”.

Material	Manufacturer (Perceived Quality)	Batch
PE	A (Low)	b-A1
		b-A2
PVC	B (Medium)	b-B1
		b-B2
	C (High)	b-C1
		b-C2

Considering the reported positive nonlinear correlation between surface roughness of films and oxygen and water vapour permeability [8,9], a factorial design was implemented to test the effect of the main features of shelf-grade polymeric food packaging film on surface topography. Specifically, the two polymeric materials, namely PE and PVC, and three manufacturers were considered. The manufacturers were selected based on the customer-perceived quality of the shelf-grade polymeric film depending on the shelf-cost. Brand and manufactured are not disclosed, for a market comparison is considered out of the limited scope of the present work. Considering commercial availability of the considered materials, the manufacturer resulted nested in the material, and, consequently, the batch resulted nested in both the manufacturer and the material. Additional variability components were included in the factorial design, to gather further insights into factors possibly impacting on the permeability of the film. Specifically, manufacturing reproducibility is considered by testing one product from 2 batches per manufacturer. The resulting nested factorial design, summarized in Table 2, consisted of a 2×3×3=18 measurements per measuring instrument, and was analysed by means of Generalized Linear Model (GLM) to investigate factors-induced significant systematic effect on the evaluated surface topography parameters [22].

Results and Discussion

Fig. 1 shows pseudo-colour surface topographies measured for the three manufacturers. As it can be qualitatively appreciated, CSI measurements present a range of surface heights larger than one order of magnitude. This is due to the fact that the larger field of view of CSI inherently caters for the topography shape, here represented by residual wrinkles of the surface. Conversely, the AFM measurement shows a highly isotropic surface, which was also confirmed by the phase signal. ANOVA performed by GLM confirmed the difference induced by the measurement length scale is systematic with a p-value < 0.001 for all the considered surface topography parameters. Accordingly, to gather more insights the two measurement length scales were then further analysed separately.

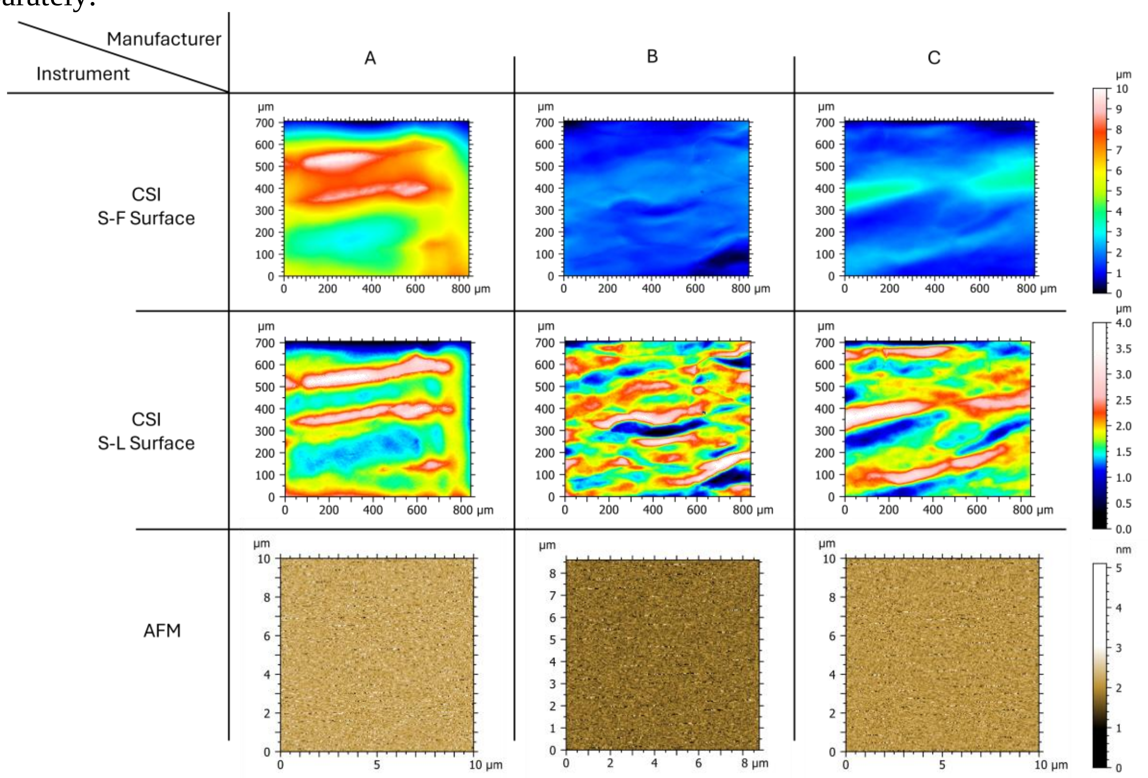

Fig. 1 *Pseudo-colour views of measured surface topography for the examined instrument-manufacturer configurations. Only one batch and one replication are shown for each configuration. CSI measurements report both S-F (nesting index 2.5 µm) and S-L surface (nesting index 0.25 mm). For AFM, levelled surface is shown.*

Considering a greater measurement area, by CSI, the material was marginally significant (e.g., requiring varying and as high as 12% risks of error) and the GLM was weakly informative, presenting a coefficient of determination R^2 lower or equal than 60% (see Table 3). The large part of not explained variability can be due to the wrinkles and remaining shape of the topography after the mounting. Conversely, as shown in Table 3, localized measurements obtained at nano-scale thanks to AFM are adequately explained by the considered factors, presenting GLM R^2 of about 90%. Surface extreme height parameters (Sv and Sz) variability was not explained by the considering factors, suggesting a main contribution from the measurement noise. For other surface topography parameters, a highly significant effect introduced by the material could be appreciated. The effect of measurement length scale and greater significance of AFM highly localized and spatially resolved measurements provide a formal motivation to the AFM use for food packaging film characterization as a literature best practice [9].

Table 3 *p*-values and coefficients of determination (R^2) for the considered factors effect on surface topography parameters at micro- and nano-length scale (respectively CSI and AFM). Factors in brackets indicate nesting.

	CSI				**AFM**			
	Material	**Manufacturer (Material)**	**Batch (Material, Manufacturer)**	**R²**	**Material**	**Manufacturer (Material)**	**Batch (Material, Manufacturer)**	**R²**
Sa	0.055	0.344	0.147	0.50	<0.001	>0.99	0.028	0.89
Sq	0.069	0.423	0.112	0.50	<0.001	0.834	0.1	0.92
Sv	0.044	0.942	0.177	0.48	0.805	0.102	0.824	0.26
Sz	0.075	0.242	0.18	0.48	0.357	0.267	0.813	0.21
Sdq	0.031	0.122	0.073	0.60	<0.001	0.566	0.006	0.96
Sdr	0.116	0.252	0.197	0.45	<0.001	0.605	0.006	0.96

Fig. 2 reports main effect and interaction plots for Sq. Trends are similar for other parameters, and considering the reported correlation between the gas permeability and transmission rates and Sq, further discussion is focused – for sake of brevity – solely on the root mean square height. Both measurement scales – despite the smaller statistical difference for the micro-scale – indicate a significantly smaller surface roughness for PVC. This is well in line with the expected better barrier property, i.e., smaller P and TR, of PVC than PE, as summarized in Introduction and in Table 1. From a manufacturing perspective, the poorer permeability of PE is compensated – to respect regulatory requirements – with a thicker film. In fact, confocal microscope measurements showed that the PE thickness is 1.5 µm systematically larger than PVC films (*p*-value of 0.012 with a t-Student test).

Table 4. Six-sigma intervals for the considered surface topography parameters for the investigated materials.

Material	**Sa / nm**	**Sq / nm**	**Sv / nm**	**Sz / nm**	**Sdq / -**	**Sdr / %**
PE	0.173±0.004	0.241±0.006	1.982±0.245	4.132±0.621	9e-3±7e-5	4e-3±6e-5
PVC	0.164±0.002	0.226±0.002	1.955±0.188	3.953±0.218	9e-3±7e-5	4e-3±6e-5

Although the nested design did not allow to test significance of interactions, interaction plots provide a qualitative insight into their effect on topographical parameters, and consequently on permeability. In particular, it allows appreciating the greater stability of AFM measurements, which are less sensitive to shape variation, and show that (as confirmed by the GLM ANOVA) despite the different market positioning and cost-perceived quality, no statistically significant differences could be appreciated between the PVC-based films. Interaction plot, also show a quite large, difference between the batches of the same manufacturer, which – in some cases – was also confirmed by the ANOVA in Table 3. Thus, Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy was performed to investigate material homogeneity between batches. Results in Fig. 3 shows that only the lower quality PVC (B manufacturer) has a poorer control over material composition, which though (see interaction plots in Fig. 2) does not affect the surface topography. Conversely, the greater between-batch variability for manufacturer C cannot be ascribed to compositional differences and shall be traced back to measurement complex reproducibility. Finally, six-sigma intervals for the considered topographical parameters is evaluated, according to GLM results, per each material class. Results are summarized in Table 4.

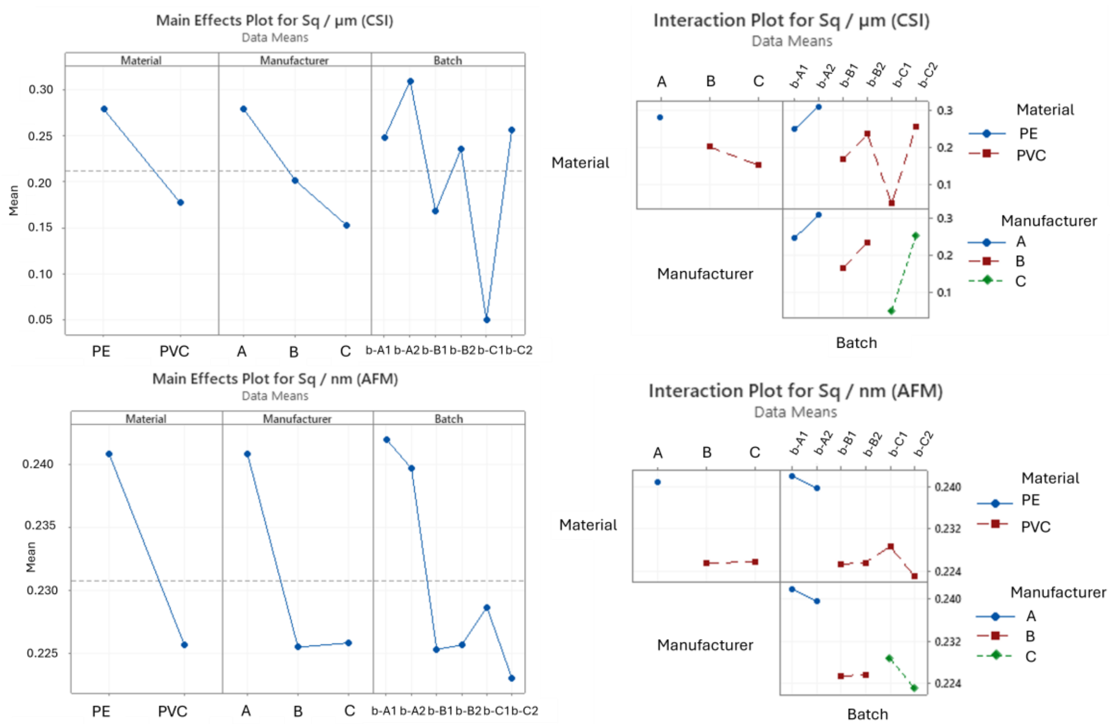

Fig. 2 *Main effects (left) and Interaction plots (right) for Sq. Top row: CSI, bottom row AFM.*

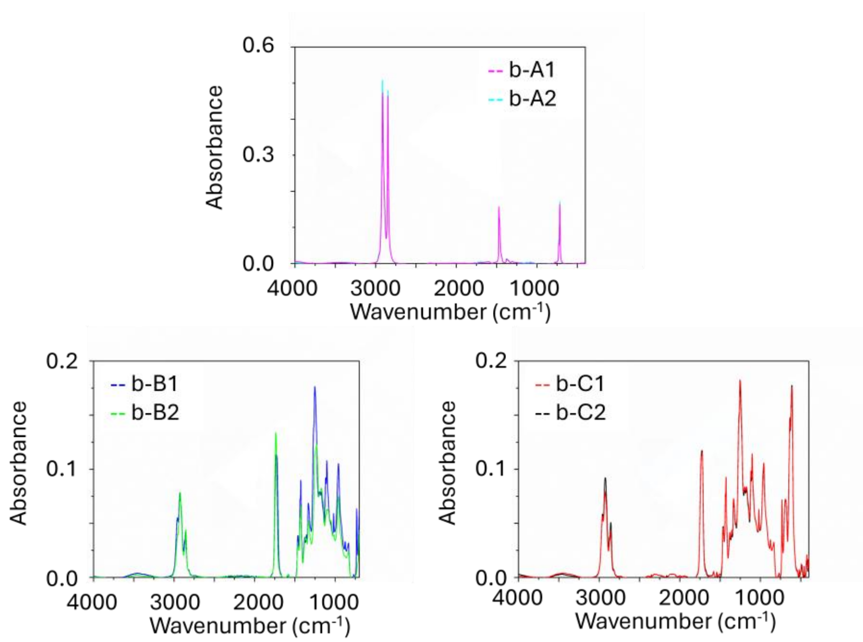

Fig. 3 *ATR-IR spectra of the six samples (two batches per three manufacturer). The lower quality PVC (manufacturer B) shows a greater variability of composition (notice the difference between b-B1 and b-B2).*

Conclusions

This work investigated methods to characterize the surface topography of polymeric films for food packaging. Surface topography is correlated to films barrier properties, which is an essential functional feature to guarantee safety and integrity of the food and extend its shelf life. This work investigated the capability of surface topography measuring instruments as an alternate indirect route for permeability quality control, representing a faster and cost-effective solution to conventional standard solutions. The results showed the relevance of the selection of the correct characterization scale. In particular, AFM provides high-resolution insights into nanoscale surface morphology providing results more robust to film topographical shape suitable for studying the interplay between topography and permeability. The investigation carried out on commercially available polymeric films showed that in some cases, the customer perceived quality – linked to similar material processed by different manufacturers - do not translate into improved functional performances. The findings of this study will contribute to the development of more efficient quality control methodologies for food packaging applications, offering manufacturers a reliable and practical means of assessing material performance. In particular, future works will calibrate the correlation between the surface topography parameters and permeability to enable faster quality control inspection procedures based on AFM measurements.

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