Permeation of vegetable oils and slippery properties of extrusion coated paperboard

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Abstract
Due to the ability of oils to penetrate into the structure of polymers, it is possible to create slippery surfaces with low water droplet sliding angles based on polymer coatings. Polylactic acid, polybutylene succinate and low-density polyethylene extrusion coatings were used as such surfaces in this study. The process of penetration of vegetable oils into the polymers was studied with the subsequent investigation of slippery behaviour of such system. Cottonseed oil and castor oil showed promising properties as lubricants. For oil infused polymer surfaces the water droplet sliding angles were significantly lower than for the untreated extrusion coating. The penetration of the permeant into the upper layers of the coating was confirmed by alteration of the static water contact angle, sliding angle and also by the cross section images. LDPE extrusion coating infused with castor oil showed the lowest water sliding angle – 8°. Biopolymers, being a main focus in this study, exhibited also promising results, PLA reached sliding angle of 14° with both olive and castor oil. Dependence of polymer permeability on various factors is rather complex and the wide range of oils used in this work helps to interpret the barrier performance of the studied materials. Degree of bond saturation, viscosity and polarity were found to influence mostly on the oil permeation through the studied polymers.

KEYWORDS
biopolymer, extrusion coating, grease barrier, lubricant infused slippery surface, oil permeation, vegetable oil

1 | INTRODUCTION

The question of surface slipperiness and adhesion is widely discussed in many publications. Low adhesion materials can potentially solve many challenges, including, surface icing or frosting, biofouling, promote self-cleaning and self-healing properties. Slippery surfaces are able to repel various liquids, thus they can also find their application in the field of packaging industry, both outside and inside a package. On the outside surface, such systems can prevent wetting and contamination, and on the inside, they can provide a more efficient or complete removal of the product. Reduced adhesion and improved slippery properties can result in product economy and also have a positive effect on the packaging material recycling process. Notable examples of such systems are slippery liquid-infused porous surfaces (SLIPS) which were presented by the Eisenberg group in 2011. In case of SLIPS, drop of liquid does not stick to the surface but is sliding even at a slight inclination. SLIPS can be described as solid–liquid system, consisting of a nanotextured substrate and a lubricant, which generally can include ionic liquids, vegetable or synthetic oils, such as silicone oil, perfluorinated oil, cottonseed, olive, coconut oils and...
rapeseed oil. Nanotextured structure required for SLIPS can be achieved by various methods, for example, by sputtering, lithography or sol–gel methods. Unfortunately, these methods are difficult to utilize in packaging technology, furthermore, nanoparticles from the texture and excess lubricant can contaminate the product.

Another approach to creating slippery surfaces is utilizing the ability of polymers to absorb oils. It is known that many polymers have certain permeability to gases and other molecules. In packaging technology this effect tends to be avoided by utilizing polymers with improved barrier properties or multilayer structure. In case of oil absorption by the polymer, the lubricant is distributed inside a substrate matrix as it was described in publication by Mukherjee et al. In that study extruded hydrocarbon-based polymer films were impregnated with lubricating oil to gain slippery properties. Impregnation was enabled by utilizing ultra low-density polyethylene (ULDPE) in combination with vegetable oil that exhibit high chemical compatibility with the polymer film. The wicking rate of the oil into hydrocarbon-based polymers is expectedly extremely low; nevertheless, it is sufficient to provide slippery properties after removing excess lubricant from the surface.

The aim of the current study is to view more comprehensively the process of wicking or penetration of vegetable oils into polymers with the subsequent investigation of slippery properties of such system. In this work, extrusion coating on paperboard was used as a substrate to mimic the real packaging unit. Such polymer coating on top of fibrous materials, paper or paperboard, has been used for a long time due to the low barrier properties of the latter. Paper is not only permeable to many liquids, but it also tends to swell, which negatively affects its physical characteristics. Generally, barrier properties of polymers against oil penetration are examined with the aim of preventing scalping. Grease barrier of polymer extrusion coatings is not well studied in literature in the context of the wide range of oils.

This work deals with three polymers which are used in packaging technology—polylactic acid (PLA), polybutylene succinate (PBS) and low-density polyethylene (LDPE). In order to study the permeability of these polymers, various natural oils with different characteristics were used. The difference between these oils should help to interpret the barrier performance of studied material and determine the possibility of manufacturing slippery surfaces based on the effect of oil penetration into the polymer structure. The combination of degradable bio-polymer and natural oil as a lubricant can potentially provide alternative approach for a recyclable packaging.

1.1 | Factors affecting infusion of oils into polymers

In order to characterize the polymer infusion with vegetable oils, it is important to study polymer permeability, which is closely connected to the barrier properties.

The barrier property of a material indicates its resistance to permeation of foreign molecules. Permeation is a combination of diffusion and solubility. The diffusion coefficient, D, corresponds to the speed of molecules moving in the polymer and the solubility coefficient, S, corresponds to the quantity of permeant molecules that are diffusing. Together, the diffusion coefficient and the solubility coefficient describe the permeability coefficient or permeability.

A permeant molecule moves through a polymer film in a multistep process: the molecule collides with the polymer surface, absorbs and dissolves into the polymer mass, permeates through polymer film, desorbs and moves away.

Below are the general factors that affect permeation process in polymers:

1.1.1 | Temperature and humidity

Permeability, diffusion and solubility coefficients follow a van't Hoff–Arhenius relationship. Consequently, increase of temperature will typically cause the decrease of barrier properties. Humidity affects some polymers as it can cause swelling or hydrolyses. In those cases, sorption of water vapour results in change in permeability, as compared to dry conditions.

1.1.2 | Properties of the polymer

Morphology

Morphology refers to crystallinity, orientation and free volume of polymer. It is generally considered that barrier failure in polymers is related to amorphous zones since diffusion and sorption occur mainly through the amorphous phase and not through crystals, the latter are supposed to be impermeable (or permeable only for such small molecules like helium). Thus, the barrier properties depend on the degree of crystallinity of the polymer and the reason firstly is the amount of the amorphous phase. Secondly, the confinement generated by the specific orientation of the crystals increase the tortuosity for the diffusing molecules. It is worth mentioning that here polyolefins are exceptions because they can possess considerable crystallinity and at the same time high diffusion coefficients.

However, crystallinity is an overrated contributor to barrier in polymer films. The degree of crystallinity in most cases is not a strong design parameter because it often can be adjusted within a narrow range during the extrusion coating process. Moreover, the same process parameters which usually increase crystallinity also lead to efficient or close packing in the amorphous phase, which lowers the diffusion coefficient. For example, it was reported that for PLA the degree of crystallinity had no effect on the helium and oxygen barrier properties. On the other hand, with an increase in size of the diffusing molecules, the constraining effect of crystallites tends to rise.

Another factor that is included in polymer morphology is orientation which involves chain alignment or chain symmetry. Orientation denotes bonding groups approaching each other to the distance of the best interaction, enhancing the tendency to form well-ordered materials (e.g., biaxially oriented polypropylene).
Glass transition temperature \( (T_g) \)
The glass transition temperature of the polymer has a certain effect, as above \( T_g \) the polymer chains are more flexible and mobile. Free vibrational and rotational motion of polymer chains occur, so that different chain conformations and orientations can be assumed.\(^{14,17}\)

It was reported that glassy polymers, for instance, polyethylene terephthalate \( (T_g \approx 69–85{\degree}C) \), have very low diffusion coefficients for big permeant molecules, for example, organic solvents.\(^9\) Polyolefins, in ambient conditions being well above their glass-transition temperature, are non-glassy polymers and have high diffusion coefficients for organic permeants. Moreover, a steady-state permeation is established quickly in such structures.\(^{18}\)

Crosslinking
Speaking about the chemical structure of the polymer, crosslinking should be also mentioned as a factor that reduces the mobility and flexibility of the system. Crosslinked polyethylene provides better barrier properties compared to uncrossed-linked one with the same degree of crystallinity.\(^{14,17}\)

Solubility parameter
Solubility parameter of the polymer plays an important role, as a rule of thumb is that ‘equal dissolves equal’. Solubility is controlled by the cohesive energy and reflects the intramolecular interactions between the polymer and the solute. To prevent massive solution of some liquid into the polymer media, one should choose the combination with very different solubility parameters. Materials with similar values of solubility parameters will tend to mutually dissolve.\(^9,19\)

Polarity
Generally, it can be considered that polarity of the polymer decreases the penetration rate. Van der Waals, hydrogen bonds or dipolar bonds lower the chain mobility and increase the energy that is needed to separate the neighbouring chains.\(^9\) However, the effect of the polarity of the polymer on its permeability also depends on the polarity of the permeant.

Plasticizers
Plasticizers are additives which are blended into polymers to improve mechanical or chemical properties such as flexibility, cling or plasticity. These additives usually are the smaller molecules that are soluble in the polymer. Plasticizers embed themselves between the chains of polymers, spacing them apart, thus affecting permeant transport.\(^{20}\) Consequently, plasticized polymer possesses increased diffusion coefficient for the permeant molecules but the solubility coefficient, however, is unaffected. The effect can be minute with minor additive concentration whereas at larger concentrations (more than 1 wt%) the effect can be significant.\(^9\)

Fillers
Fillers typically have considerable influence on the barrier performance of polymer films. Impermeable fillers, especially flat ones, improve the barrier properties by creating a tortuous path for the diffusing molecule. However, the barrier characteristics may decrease if the filler material is poorly wetted by the polymer media.\(^9,20,21\)

Molecular structure of the polymer
Stiff molecules require high energy to separate chain segments in a polymer network. For instance, replacing benzene ring with naphthene unit lowers the oxygen permeability 5 times.\(^{22}\) High molecular weight of the polymer decrease the number of chain ends, and the latter can serve as sites for permeant to be sorbed to.\(^{17,23}\)

1.1.3 | Properties of the permeant
Nature of the permeant has a significant effect on the transport properties. In this study various types of oil act as the permeants; thus, only factors that refer to oils will be discussed.

Viscosity
Viscosity is an important factor affecting the ability of the oil to spread over the surface and thereafter penetrate into polymer material. For example, it was reported that the oil diffusion rate for latexes is smaller if the viscosity is high.\(^{24}\)

Permeant molecule size
Molecule size of permeant or its carbon chain length influence on the permeation phenomenon, especially in glassy polymers. In general, an increase in the size (e.g. average diameter, molar volume) of a penetrant in a series of chemically similar penetrants leads to an increase in solubility and a decrease in diffusion.\(^{11}\) Diffusion decreases with increasing chain length apparently due to steric hindrance.\(^{17,25}\) This also concerns the permeant molecules which are not flat, but have more complicated shape, for example, spherical.\(^{26}\) On the other hand, in some studies it is stated that larger molecules are being absorbed to a greater extent than smaller ones.\(^{27}\)

Polarity of the permeant
All other things being equal, the effect of the polarity of the permeant on its diffusion performance is negative, which can probably be associated with higher cohesive forces. For instance, for similar terpenes carvone \( (C_{10}H_{14}O) \) and limonene \( (C_{10}H_{16}O) \) it was pointed out that limonene, being less polar one, permeates through polymers more efficiently.\(^{28}\) When comparing the different classes of organic compounds, a similar correlation with polarity was obtained, alcohols had poor penetration compared to less polar esters or aldehydes. Analogously, the least polar hydrocarbons showed the highest affinity for the polymer.\(^{27,29}\) However, it should be noted that these studies mostly dealt with polyolefins, thus, for other polymers, the observed dependence may vary. It is also assumed that a polar chemical will normally have a lower permeation rate in a nonpolar polymer than a nonpolar species and vice versa. The reason is the ability of chemicals with similar structures to the polymer to swell the polymer, creating space between the chains for permeation.\(^{19}\)
Unsaturated bonds

Correlation between unsaturated bonds of oil and the rate of its permeation is not well studied. It was shown that greater degree of saturation leads to faster penetration into LDPE for fatty acids. Charara et al. reported that aldehydes which had double bonds (perillaldehyde and geranial) were absorbed by polyolefins to a much lesser extent than saturated aldehyde.

The amount of saturated and unsaturated bonds in oils can be estimated by the iodine number. The higher the iodine number, the more unsaturated bonds in fatty acids' carbon chains this particular oil contains.

Solubility parameter

Solubility parameter reflects the tendency of particular liquid to solute in particular polymer and can potentially explain why for some oils the rate of penetration is greater compared to others. As it was mentioned earlier, substances that have similar solubility parameter values will tend to mutually dissolve. Unfortunately, this factor will be complicated to use in this study, because vegetable oils often have very close or almost identical solubility parameters (e.g., for linseed oil and for cottonseed oil Hansen solubility parameter is 14.9 MPa0.53).

2 | EXPERIMENTAL

2.1 | Materials

2.1.1 | Polymers

The coated paperboard samples were produced on the coating pilot line at Tampere University, Paper Converting and Packaging Technology unit. The substrate for all the samples was Cupforma Natura commercial paperboard by Stora Enso with a grammage of 195 g/m². Release paper utilized in the study was UPM SIL + HG65.

Extrusion coating was applied on one side. The polymer coating properties and extrusion parameters are described in Table 1.

Polymer materials which were utilized in the study are commercially available grades of polylactic acid, polybutylene succinate and low-density polyethylene.

PLA and PBS are thermoplastic polyesters and biopolymers which are widely used as a degradable packaging material. LDPE is a thermoplastic polyolefin and the most used polymer in packaging industry.

2.1.2 | Oils

Natural oils consist of triglycerides of fatty acids and related substances (free fatty acids, phospholipids, waxes, sterols, etc.) The properties of oil mostly depend only on the composition and position of fatty acids, as the part relating to glycerine in all oils is the same. It should be also noted that vegetable oils are derived from vegetable raw materials; consequently, chemical composition can vary depending on the type, quality or place of origin of the plant.

A number of factors affect the penetration of liquids into the polymer; thus, a wide range of natural oils with different characteristics was investigated in this study (Table 2). Oils included in this study are widely used in food or cosmetic industry. Both vegetable and synthetic oils (silicone oil, 50 cSt) were purchased from Sigma-Aldrich.

| TABLE 1 | Properties of extrusion coating polymers9,32 |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Polymer | Formula | Density, g/cm³ | Glass transition temperature, °C | Coating grammage, g/m² | Melt mass-flow rate, g/10 min | Coating thickness, μm | Chill roll temperature, °C |
| PLA |  | 1.24 | 55 | 20 | 6 | 16.1 | 10 |
| PBS |  | 1.26 | -32 | 17 | 15 | 13.5 | 10 |
| LDPE |  | 0.923 | -120 | 12.5 | 4.5 | 13.5 | 10 |
TABLE 2  Physical and chemical properties of oils

| Oil          | Density, g/cm³ | Viscosity (20°C), mPa s | Iodine value | Melting point, °C |
|--------------|----------------|-------------------------|--------------|------------------|
| castor       | 0.952–0.965    | 935–1030                | 82–90        | –16              |
| cottonseed   | 0.916–0.918    | 80                      | 98–118       | 13               |
| jojoba       | 0.863          | 43.5                    | 82           | 7                |
| linseed      | 0.930–0.935    | 48                      | 170–204      | –24              |
| olive        | 0.909–0.915    | 80                      | 80–88        | 0                |
| peanut       | 0.910–0.915    | 78                      | 84–100       | –2               |
| sesame       | 0.921–0.924    | 65                      | 136–138      | –6               |
| almond       | 0.914–0.920    | 66–76                   | 85–106       | –20              |
| rapeseed     | 0.914–0.920    | 85                      | 110–126      | –9               |
| silicone     | 0.960          | 48                      | –           | –55              |

3  | METHODS

3.1  | Thermal analyses

Differential scanning calorimetry (DSC) was used to estimate the degree of crystallinity of the polymers. In this method only extrusion film samples without a paper substrate were investigated. In order to receive these samples, sheets of release paper were attached to the paper roll on the pilot line before the extrusion coating process. After the coating procedure the resulting extrusion films can be easily removed from regions with release paper without any damage.

Thermal transitions of polymer films were investigated using a NETZSCH DSC 214 apparatus (TA Instrument). For these experiments standard 40-μl hermetically sealed aluminium crucibles were utilized, mass of the sample was nearly 10 mg for each run. PBS and LDPE were heated from 30°C to 150°C. PLA, due to its higher melting temperature, was heated from 30°C to 200°C. The heating and cooling rate were 10°C min⁻¹. For each polymer, at least four parallel tests were performed.

The degree of crystallinity was calculated from obtained data using Equation 1.

\[ \chi = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \]  

where \( \Delta H_m \) is a heat of melting and \( \Delta H_m^0 \) is the standard melting enthalpy corresponding to ideal 100% crystalline polymer (277 J/g for LDPE, 37 93 J/g for PLA, 38 110 J/g for PBS).

3.2  | Roughness measurements

The investigated extrusion coatings do not possess a special textured surface, which can affect the wettability. The roughness measurements in this study aim to observe that the LDPE, PBS and PLA surfaces are of the same smoothness, as well as to ensure that there are no protrusions, obstacles or other defects that act as pinning points for a sliding drop of water. In addition, roughness can affect the grease barrier properties of materials as it affects the spreading of the oil.

Approximately 5-cm² pieces of each sample of polymer coated paperboard were cut from the sheets and mounted on glass slides using a double stick tape. The roughness of the samples was examined with Wyko NT1100 Optical Profiling System. This device utilizes white light interferometry and allows to conduct measurements on surfaces which are difficult to evaluate with other machines, for example, transparent or white samples. Each result is an average of at least three determinations for a sample.

3.3  | Surface free energy and surface tension measurement

These experiments aimed to determine the polarity of studied materials - extrusion coatings and vegetable oils. Solid surface energy was calculated using contact angles of two different liquids according to ASTM D7490-1340 (Standard Test Method for Measurement of the Surface Tension of Solid Coatings, Substrates and Pigments using Contact Angle Measurements). This test method is based on solving Owens–Wendt–Kaelble equation:

\[ \gamma_s (\cos \theta) = \frac{1}{2} \left( (\gamma_{ld} + \gamma_{lp}) + (\gamma_{ld} - \gamma_{lp}) \right) \]  

where \( \gamma_s \) is a surface tension of the liquid, \( \theta \) is a contact angle, \( \gamma_{ld} \) is a dispersive component of surface energy for the solid, \( \gamma_{lp} \) is a dispersive component of the surface tension of the liquid, \( \gamma^{\alpha} \) is a polar component of surface energy for the solid and \( \gamma^{\alpha} \) is a polar component of the surface tension of the liquid. Analysing two liquids with known parameters it is possible to evaluate polar and dispersive components of solid surface energy. The sum of \( \gamma_{ld} \) and \( \gamma_{lp} \) values gives the total solid surface tension or surface free energy (SFE).

In this study, the following liquids were taken: diiodomethane with surface tension of 50.8 mN/m (\( \gamma_{lp} = 1.3 \) mN/m, and \( \gamma_{ld} = 49.5 \) mN/m), and water with surface tension of 72.8 mN/m (\( \gamma_{lp} = 51.0 \) mN/m, and \( \gamma_{ld} = 21.8 \) mN/m).
Contact angles (CA) of water and diiodomethane on studied polymers were determined using KRUSS Drop Shape Analyzer–DSA100 at ambient conditions of 23°C and 50% relative humidity. Minimum 5 parallel evaluations of the contact angle were conducted for each sample.

The same equation (Owens–Wendt–Kaelble) was utilized for calculation of oils surface tension and its components. To simplify the Equation 2, it is possible to remove the polar component, considering poly (tetrafluoroethylene) (PTFE) to be a standard reference surface not capable of polar interactions with liquids. Untreated PTFE is assumed to have a surface energy of 18.0 mJ/m². Thus, the dispersive component can be calculated with the Equation 3:

\[
\gamma_d = \left(\frac{\gamma_l^2}{2}\right)\cos \theta_{\text{PTFE}} + 1)^2
\] (3)

The polar part was calculated as \( \gamma_p = \gamma_l - \gamma_d \).

Polarity was calculated using Equation 4

\[
\text{polarity} = \frac{\gamma_p}{\gamma_l} \times 100\%
\] (4)

Surface tension of oils was measured using pendant drop method. In this experiment the drop of oil is hanging from the syringe needle and the shape of this droplet is regulated by the balance of forces: surface tension and gravitation. Surface tension calculations are based on Equation 5:

\[
\gamma_l = \frac{\Delta \rho g R_0^2}{\beta}
\] (5)

where \( \Delta \rho \) is the density difference between studied liquid and the surrounding medium (air), \( g \) is the gravitational constant, \( R_0 \) is the radius of curvature at the drop apex and \( \beta \) is the shape factor. To define the geometrical parameters the pendant droplet should be at its mechanical equilibrium. In order to correctly determine the surface tension, it is necessary that the drop of oil was as large as possible, but at the same time should be still hanging on the tip of the syringe needle. A detailed description of the calculation of the geometric parameters based on the drop image can be found in the literature. In this work the analyses of the shape profile of a pendant drop, as well as surface tension calculations, were performed with KRUSS DSA100 software. Each result was an average of at least three determinations for the oil sample.

3.4 Optical microscopy

The penetration of oil in the bulk of polymer was observed using optical microscopy. A small amount of dyed oil (Sudan Red, Acros) was applied on the top of the coated paperboard. Sudan Red, an oil soluble dye, was used in concentration 10 g/l providing a bright colour to the solution. After exposition time the oil was thoroughly removed with blotting paper. Penetration of dyed oil can be illustrated by the coloration of the polymer coating upon diffusion of the liquid inward. The cross sections were prepared with a Thermo Scientific Microm HM 325 Rotary Microtome. For the cross section preparation, the sample was covered with a tape, two layers to the coated side and one layer to the other side, after that it was placed between two Teflon sheets. Then the sample fixed between the Teflon sheets was inserted to specimen holder, and with hand wheel rotation it was cut until it was even. At this stage the final thickness of the cross section is adjusted. After two waste layers, the tape is placed against the sample and with accurate wheel rotation sample is cut to the tape. Tape with the sample is attached to the microscopic slide with immersion oil on it. Before placing a cover glass on top of the sample a drop of immersion oil is placed there. Excess immersion oil is pressed out a with hand paper.

Cross sections were observed using ZEISS microscope. No polarization was used when taking pictures of the sample cross section.

3.5 Grease barrier measurements

Extrusion coated paperboard was tested to study the resistance of coatings to oil penetration. Due to the fact that all coatings were applied on the same type of paperboard and all extrusion coatings have a similar thickness (Table 1), the oil penetration process is limited only by the coating material itself.

Grease barrier properties of the materials were studied according to Standard Test Method for Rate of Grease Penetration of Flexible Barrier Materials (ASTM F119-82(2015)). Sample is placed on the silica gel plate (TLC Silica gel 60 F254, Merck), then two cotton flannel disks (diameter 20 mm) on top of each other are placed on the sample surface. After that six droplets of studied liquid are applied on these disks and 50-g weights (diameter 20 mm) are placed on the top of soaked textile (Figure 1A). All the assembly is stored at elevated temperature (40°C) in the oven. The studied liquid first diffuses through the extrusion coating, then through the paperboard, and after that it reaches the back side of the sample contacting silica gel plate. Thus, the liquid wets the silica gel after its full penetration through the sample. At periodic intervals, depending on the time to anticipated failure, silica gel plate is monitored for signs of oil or grease penetration. The contact of silica gel with oil can be clearly observed in UV light by the stains on the silica gel plate, as shown in Figure 1B. Failure indicates that oil penetration through the packaging material has been detected.

Results of the experiment are expressed as the time in hours in which a test liquid has penetrated through a packaging material. Obtained data include average hours to failure, the minimum and maximum hours to failure for each sample. For each sample polymer, from six to eight sites were examined.

Unfortunately, this method does not allow to study the permeation of silicone oil into polymers, since silicone oil does not provide a representative colour change in UV light. Therefore, it is impossible to
determine the moment when the oil leaked through the polymer layer and paperboard substrate.

### 3.6 Preparation of oil infused polymer coatings

Oil was applied on the top of the polymer surface with a pipette, then a thin layer of oil was formed as a result of gravity-induced spreading. In cases where a uniform spreading was too slow (high viscosity liquids), the oil was distributed with a brush.

The samples with oil layer were stored overnight at 40°C, as the elevated temperature will accelerate the permeation process. It is also important that this temperature was equal to the temperature of the grease barrier tests.

After exposition time the samples were cleaned with the blotting paper, the oil was removed thoroughly until oil traces are invisible. At this stage samples were weighted to determine the amount of oil that has permeated to the surface layer of the polymer coating. For some samples additional cleaning stage was performed—the surface was cleaned with 96% of ethanol to ensure that residual oil contamination was eliminated. Before wetting measurements, the samples were stored for 24 h in a climatic room (23°C and 50% relative humidity) for conditioning.

### 3.7 Contact angle and sliding angle measurement

The static contact angles and the droplet sliding angles were measured using a KRUSS Drop Shape Analyzer–DSA100 at ambient conditions of 23°C and 50% relative humidity. Oils, extrusion coated paperboard samples, as well as PTFE, were stored in ambient conditions at least 24 h prior tests. PTFE is a non-conductive material; thus, an uneven static charge can remain on its surface and this leads to distortion of the droplet shape. Therefore, to determine the oil wetting angle on PTFE, special attention was paid to the droplet symmetry. Only droplets with similar left and right wetting angles were analysed. The determination of the static contact angle was performed after 3 s since the droplet deposition.

Measurements with tilting table were conducted to detect the sliding angle (SA) values. The tilting speed for the experiments was relatively low (10° per minute) in order to capture the moment of droplet motion. A faster tilting was used in cases when the droplet does not move at large angles (e.g., when testing pristine extrusion films). Then the tilting rate was doubled to avoid a long-term experiment that would lead to a significant change in droplet volume due to evaporation. The tilting of the table was initiated after 3 s since the droplet deposition. Sliding angle was identified as an angle at which the surface should be tilted for the beginning of the constant motion of the droplet. The number of independent measurements for experiments was 10 or more. The droplet volume was 6 μl for static contact angle measurements and 10 μl for the experiments with tilting.

### 4 RESULTS AND DISCUSSION

#### 4.1 Differential scanning calorimetry (DSC)

A large number of the polymers used in packaging technology are semi-crystalline; that is, they contain both amorphous and crystalline phases. The manufacturer of plastics (pellets) for extrusion generally provides the information about material properties including the degree of crystallinity. However, the properties of a polymer film can vary because melting and crystallization/vitrification occur in the extrusion process. PLA biopolymer is a semi-crystalline polymer with relatively slow nucleation and crystallization rate. As a result, most extruded objects from these grades such as sheet and pellets are expected to be amorphous after normal quenching operations. PBS and LDPE are expected to have higher crystallinity. The calculated degree of crystallinity for utilized polymers is 1.3 ± 0.4 for PLA, 59.9 ± 2.2 for PBS and 41.1 ± 2.2 for LDPE.

#### 4.2 Roughness of extrusion coating

For extrusion coating similar process parameters were used for all the polymers, consequently this should have led to a similar surface roughness. Chill roll affects the roughness most significantly; in current case chromium plated glossy chill-roll was used for all polymers.

Based on the measurements, the utilized polymer coatings have quite similar roughness (Rₐ): 396 ± 60 nm for PLA, 198 ± 60 nm for
PBS and $425 \pm 60$ nm for LDPE. It can be considered that the surface is sufficiently smooth, and the difference in wetting and slippery properties for different polymers is not related to the roughness. Also, no significant defects that can reduce sliding properties were detected.

In this case, the roughness is not hierarchical and does not have the particular structure, which is a necessary condition for providing Cassie–Baxter state and, consequently, superhydrophobicity.

4.3 | Surface free energy of polymers

The study of the polarity of the polymer and the penetrating liquid is interesting from the point of view of the interpretation of the grease barrier performance. As discussed before, it is believed that more polar oils penetrate better into more polar polymers, and vice versa.\textsuperscript{19}

LDPE, PLA and PBS are quite common polymers, thus data from previous studies is also presented for comparison with obtained data (Table 3).

Based on the experimental data, PLA and PBS are more polar materials, compared to polyethylene, which is a non-polar polymer. The reason of the increased polar part is the presence of oxygen containing functional groups in these biopolymers. Obtained result is in agreement with previous studies but the actual values are somewhat different. The surface properties of a polymer undergo certain changes over time, so it was important to study the specific coating samples.

4.4 | Surface tension and polarity of oils

The polarity of oils is one of the factors that affect the penetration through the polymer coating. Vegetable oils are considered to be relatively non-polar compounds; however, synthetic oils such as silicone or mineral oils (aliphatic hydrocarbons) are much less polar.\textsuperscript{48}

Figure 2 shows the experimentally obtained surface tension of vegetable oils, as well as the calculated polar and dispersive components. All the values, including standard deviations, are also provided in Table S1.

The polarity of a liquid depends on the ratio between the dispersive and polar components of surface tension. As expected, castor oil, which contains a large number of hydroxyl groups, has the highest polarity. Sesame oil also showed high polarity. Jojoba oil, on the contrary, eventuated to be the most non-polar.

4.5 | Cross section

Several cross sections of extrusion coated paper were studied with optical microscope. All polymer coatings look white or colorless in the cross sections, but the regions with diffusion of dyed oil have a considerable difference in outlook (Figure 3).

Experiments were conducted with castor oil, cottonseed oil and silicone oil. In case of cottonseed oil, the appearance of colour is visible already after 20-min exposition time for LDPE and PBS. For PLA these changes were not so significant, because of the higher grease barrier properties, compared to PBS and LDPE. Other oils showed less rapid penetration, however, in case of, a noticeable staining of the polymer coating could be also observed. It should be noted that such experiment cannot provide any accurate quantitative data on the diffusion of oils into the polymer. The penetration of oil into the polymer is uneven and it is difficult to observe the diffusion front. However, the presence of staining illustrates the phenomenon of penetration.

4.6 | Rate of oil penetration

PLA and PBS are considered to have good barrier properties against gases and grease; moreover, commercially available PLA films can provide functional properties comparable to those of polyethylene terephthalate.\textsuperscript{49} Polyoilefins, as LDPE, generally are not classified as high-barrier polymers. They form good barriers against water and water vapour but are relatively permeable to gases, oil and grease. The diffusion of oil into the polymer depends on both the properties of the polymer itself and the physical and chemical properties of the oil (Table 2). Obtained data for rate of oil penetration for three extrusion coatings are presented on Table 4.

PLA, generally providing good grease barrier, expectedly shows significant resistance to oil penetration. LDPE has relatively poor grease barrier performance. It should be noted that according to DSC measurements the degree of crystallinity of PLA coating is quite low. Consequently, in this case, resistance of the material to oil penetration was ensured by a PLA consisting mainly of an amorphous phase. However, in general, the effect of crystallinity should only be assessed when comparing the same types of polymers. PBS coating consists mainly of a crystalline phase, but it did not provide efficient grease resistance.

Unfortunately, this makes it difficult to estimate the regularities in penetration of individual oils. Thus, for the analysis of the permeability of polymer coatings with various vegetable oils, it is

| Polymer | Obtained data, mN/m | Data from literature, mN/m$^{45-47}$ |
|---------|-------------------|----------------------------------|
|         | SFE | Dispersive part | Polar part | Polarity % | SFE | Dispersive part | Polar part | Polarity % |
| LDPE    | 29.3 ± 0.8 | 28.4 ± 0.5 | 0.9 ± 0.3 | 2.9 | 25.9 | 25.9 | 0 | 0 |
| PLA     | 41 ± 1.6 | 35.5 ± 0.8 | 5.5 ± 0.8 | 13.4 | 41.6 | 30.8 | 10.8 | 26.0 |
| PBS     | 41.5 ± 1.6 | 35.6 ± 1 | 5.9 ± 0.8 | 14.2 | 43.7 | 40.4 | 3.3 | 7.6 |
convenient to normalize the ‘hours to failure’ parameter. For each polymer, the average value for the penetration (in hours) of rapeseed oil was taken as one unit. The normalized values for the remaining oils were calculated as the average ‘hours to failure’ ÷ average ‘hours to failure’ for rapeseed oil. The result of normalization is shown in Figure 4.

Certain similarities in the diffusion of vegetable oils can be distinguished from Table 4 and Figure 4. Linseed oil penetrates through the polymer structure the fastest. For PBS and LDPE, linseed oil permeates through the entire polymer layer in just a few hours. For PLA, this process was not so prompt, but nevertheless much faster compared to other oils. Presumably, linseed oil penetrates so quickly through the LDPE layer due to the fact that it participates in some kind of chemical reaction with polymer. There is some evidence of the mediocre chemical resistance of LDPE to linseed oil; however, this applies only to some brands and at elevated temperatures (60°C).19 However,
generally, a good chemical resistance of polyethylene to vegetable oils, in particular to linseed oil, is reported.

According to Table 2, a distinctive feature of linseed oil, in comparison with other oils, is a high iodine value, which indicates a high number of unsaturated bonds in the fatty acid carbon chain. Linseed oil comprises a significant amount of triply unsaturated \(\alpha\)-linolenic acid. Thus, it can be supposed that oils with mostly unsaturated fatty acids diffuse more actively into the polymer. Cottonseed oil, which showed a fairly fast diffusion for all polymers, also contains a large amount of polyunsaturated bonds (linoleic acid).

At the same time, the lowest iodine values refer to castor oil and jojoba oil. Polymer extrusion coatings, when tested with these oils, showed a considerable amount of ‘hours to failure’.

Figure 5 shows the influence of the oil polarity and iodine value on the rate of its penetration into the polymer coating. Average values of iodine value and calculated polarities were used in the comparison.
The complexity of analysing the influence of polarity and bond saturation is linked to the fact all the factors are cross-affecting and in this case, it is complicated to exclude one or several of them. As a result, the points are scattered due to the multifactorial nature of the system, but linear trend estimation visualizes the general tendency. For iodine value a downtrend is observed for all polymer coatings. The higher the iodine number (unsaturated oils), the faster the oil penetrates into the polymer structure. Consequently, oils with a large number of saturated bonds penetrate the polymer coating slowly.

Concerning polarity, it is assumed that non-polar liquids penetrate better into a non-polar media (equal dissolves in equal). Accordingly, the trend for non-polar LDPE is that the greater the polarity of the oil, the slower it penetrates into the polymer. PLA and PBS are more polar polymers; therefore, such an upward dependence is not pronounced for them.

Analysing the properties of oils (Table 2) and their penetration through polymers, special attention should be paid to castor oil, which is quite exceptional compared to the rest. The viscosity of castor oil is an order of magnitude higher than that of the other oils, and this affects its interaction with polymers. Castor oil contains mainly glycerides of viscous ricinoleic acid. The ricinoleic acid forms approximately 90% of the total fatty acid content in castor oil and the hydroxyl group that is contained in that acid has a great impact on the physical properties resulting in high viscosity and polarity.

Unfortunately, it is difficult to study in more detail the influence of the viscosity of vegetable oils on their permeation into the polymer coatings. In addition to viscosity, multiple oil properties affect the permeation. Varying temperature when studying barrier properties to change oil viscosity is also not an appropriate solution, because temperature affects not only the viscosity of the oil but also the properties of the polymer. As the temperature rises, the polymer chains become more flexible and mobile. Temperature significantly influences the grease barrier properties of the polymer; because permeability, diffusion and solubility coefficients follow the Arrhenius equation as it was discussed above. Finding two oils with identical parameters, but with different viscosities, is challenging.

Thus, most likely, both polarity and viscosity are the reasons for the delayed castor oil penetration into all extrusion coatings in this study. Furthermore, the relative rate of penetration of castor oil into non-polar polyethylene is somewhat lower, compared to slightly polar PBS and PLA (Figure 4).

Jojoba oil, in contrast, occurred to be one of the least polar oils, according to the experimental data. Analogously, its penetration into more polar PLA and especially PBS is quite slow, while non-polar LDPE showed rather low barrier performance against jojoba oil.

4.7 Slippery properties of the infused extrusion coatings

In the previous part of the study, it was shown that all tested vegetable oils penetrate into polymer coatings, but at different rates. Penetration into LDPE was relatively fast, and the PLA showed the highest grease barrier performance. In order to improve the sliding characteristics, it is sufficient to infuse with lubricant only the surface layers of the polymer. On the other hand, from the point of view of utilizing the extrusion coating as a kind of oil reservoir to prevent depletion of the surface layer, a significant permeation of oil into the polymer is preferred. In the process of preparing of oil infused polymer coatings the same exposure time was used for all materials, corresponding to the following tasks:

- the lubricant must penetrate at least into the surface layers to provide a slippery surface;
- at the same time, the exposition period should not be too long in order to prevent failure of the sample, for example, penetration or leakage of oil through both the polymer and the paperboard layer.

Linseed oil showed the highest rate of penetration into all polymers studied, but its use for lubricant infused slippery surfaces seems questionable. Linseed oil is oxidized rather quickly in air and forms a polymer film, in other words, it dries out. Oxygen in the air contributes to the formation of conjugated systems of unsaturated bonds and further polymerization of fatty acids, especially, at elevated temperatures. Oils with high iodine values, as linseed, are considered drying oils; they oxidize in air, form resin-like elastic films, insoluble in organic solvents.

Oils that have none or minor amount of double or triple bonds in the structure are considered non-drying (e.g., olive, peanut, jojoba and castor). Such oils are quite stable; they do not react with oxygen in the air and do not form polymeric films when heated. It is beneficial to choose lubricant that is chemically inert and provides a long and uniform sliding performance. Lubricant should not react with the environment or substrate and preferably not dry out.

For the analysis of infused slippery surfaces as a system of extrusion coating and lubricant, the following oils were selected: cottonseed (as it showed a high rate of penetration into the polymer), castor (low rate of penetration), olive (medium rate) and silicone (as an example of a synthetic oil). By weighing the samples before oil application and after removing it from the surface, approximate amounts of oil penetrated into the polymer material were obtained (Table S2). According to the experiments, 0.75 g/m² for castor oil and 0.24 g/m² for cottonseed oil remained impregnated into the polymer coating. These data correlate with previously published values.

The static water contact angle for polymer coatings corresponds to the polarity of the polymers: LDPE is a non-polar polymer, unlike PLA and PBS. Water sliding angles for all coatings before contact with oil are similar to each other—water droplet remains motionless on the surface at an inclination more than 45°.

The results of sliding properties of oil infused extrusion coatings are presented in Table 5. Low sliding angles are preferable as this indicates that the water droplet is removed from the sample surface with a minor inclination, which corresponds to low adhesion to the surface.
The samples were divided into two categories. For one group, the removal of oil from the surface was performed only with blotting paper until the visual absence of the oil traces. For second group, the surface was additionally cleaned with a blotting paper moistened with ethanol. This helps to ensure that the slippery properties of the samples mostly correspond to the absorption of the lubricant and not to oil residue on the surface.

After penetration of oil into the polymer structure, the sliding properties change drastically. Despite the absence of extra lubricant on the surface, some samples have a sliding angle of less than 10°. For samples that were additionally cleaned with ethanol, the sliding angles are higher. However, their sliding performance still significantly exceeds sliding performance of dry or uninfused polymers. It was also observed that after removing the oil from the surface, the coatings became matt, but in some exposure time, they visually retrieve gloss. Oil diffuses from the bulk back to the surface area, providing lubrication and allowing the water drop to slide easily at low angles.

Cottonseed oil and castor oil showed optimal lubricant performance. Castor oil significantly improved sliding characteristics, despite the slowest penetration rate into the polymer. An interesting effect was observed for silicone oil, although the sliding angles for the infused samples were not so low, but the droplet speed was higher than for vegetable oils due to the great lubricating properties of the silicone oil. For LDPE, a significant decrease in the sliding angle is observed with almost all oils, which correlates with the results of barrier tests. This polymer showed low barrier for oils, in other words, the penetration of the lubricant into the LDPE is relatively quick. However, biopolymers also show improved slippery properties, for example, PLA with olive, cottonseed and castor oil.

### TABLE 5 Sliding properties of oil infused extrusion coatings

| Extrusion coatings                  | PBS  | PLA  | LDPE |
|-------------------------------------|------|------|------|
| **Static water CA**                 |      |      |      |
| SA on dry film                      | 67 ± 1.5 | 73 ± 1 | 97 ± 1.5 |
| **Static water CA after oil infusion** |      |      |      |
| Olive oil                           | 82.5 ± 1 | 81 ± 2 | 86.5 ± 1.5 |
| Castor oil                          | 71.5 ± 1.5 | 71 ± 1 | 75 ± 1 |
| Cottonseed oil                      | 76.5 ± 1 | 82 ± 3 | 87 ± 1 |
| Silicone oil                        | 85 ± 1 | 87 ± 1 | 104.5 ± 1 |
| **SA after oil infusion**            |      |      |      |
| Olive oil                           | 30 ± 6.5 | 14 ± 3 | 42 ± 4.5 |
| Castor oil                          | 23 ± 1.5 | 14 ± 1.5 | 8 ± 1.5 |
| Cottonseed oil                      | 23 ± 4.5 | 20 ± 4 | 9 ± 3 |
| Silicone oil                        | >45 | 23 ± 3.5 | 27 ± 3 |
| **Static water CA after oil infusion (cleaning with EtOH)** |      |      |      |
| Olive oil                           | 80 ± 1.5 | 74 ± 2 | 90 ± 1.5 |
| Castor oil                          | 72.5 ± 1 | 74.5 ± 1 | 76 ± 1.5 |
| Cottonseed oil                      | 75 ± 1 | 80 ± 2 | 90.5 ± 2 |
| Silicone oil                        | 81 ± 1.5 | 84 ± 1 | 104 ± 1 |
| **SA after oil infusion (cleaning with EtOH)** |      |      |      |
| Olive oil                           | 31 ± 6.5 | 22 ± 2 | >45 |
| Castor oil                          | >45 | 31 ± 6.5 | 20 ± 6 |
| Cottonseed oil                      | 36 ± 6 | 24 ± 2.5 | 16 ± 2 |
| Silicone oil                        | >45 | 40 ± 6 | 27 ± 3 |

### 5 CONCLUSIONS

This study provides useful data to predict vegetable oil penetration through the extrusion coating. A wider range of polymers should be investigated to more fully assess the effect of polymer chemistry and physics on its permeability.

Overall, the observed results support the hypothesis of the influence of polymer and permeant polarity that a polar liquid generally has a lower penetration rate in a non-polar polymer compared to non-polar liquid, and vice versa. Oils with mostly unsaturated fatty acids diffuse more actively into the polymer. Linseed oil, having a large number of unsaturated bonds (and consequently high iodine value), penetrated into the polymer structure faster, whereas mostly saturated jojoba oil showed low rate of penetration.

These dependences were observed for all investigated polymer coatings; however, it is difficult to assert the clear impact of these properties due to the number of cross-affecting factors.

The high viscosity and polarity of the oil hinders its penetration, as in case of castor oil.

Most of the studied polymer coatings with oil infusion showed improved slippery properties, even after cleaning the surface with ethanol. LDPE extrusion coating infused with castor and cottonseed oil showed lowest water sliding angle of 8° and 9°, respectively. Biopolymers, being a main focus in this study, exhibited also promising results: PLA reached sliding angle of 14° with both olive and castor oil. Analysis of the data revealed that combination of the tested polymer coatings with cottonseed oil is optimal in terms of penetration rate and slippery performance.
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