

Esters of α -1,3-glucan: designed enzymatic polysaccharides as new matrices for sustainable packaging and membrane applications

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ABSTRACT

Enzymatic polymerisation of sucrose creates nature-identical polysaccharides, such as poly α -1,3-glucan, offering a scalable approach to introduce biopolymers into industrial applications. In this study, we explored the solubility, diffusivity, and permeability of various fluids (CO_2 , O_2 , liquid and vapour water) in films of α -1,3-glucan and its long-chain acid esters, specifically two glucan palmitates (GP) and one glucan laurate acetate (GLA) with varying degrees of substitution (DoS), highlighting the potential of glucan derivatives in packaging and membrane separation applications. Additionally, we evaluated films' wettability through contact angle measurements and examined dimethyl carbonate as an alternative to chloroform for film production. GP2, the ester with the highest degree of substitution studied here, reached water uptake of $\sim 2 \text{ g mm}^{-2} \text{ day}$ at 100% RH, which is 400 times lower compared to the unmodified glucan. CO_2 and O_2 permeability exhibited patterns seen in cellulose esters, with GPs showing CO_2 permeability levels higher than 100 Barrer ($3.34 \times 10^{-14} \text{ mol m/(m}^2 \text{ s Pa)}$), promising for CO_2 separation in membrane processes. A quantitative correlation between water uptake in glucan- and cellulose-based materials and their structure is provided as a first tool to assess applicability of these materials in processes where water transport is a key factor.

1. Introduction

The introduction of biopolymers in different fields is of increasing interest for industrially relevant applications and processes, such as membrane separations, packaging etc. (Mangaraj et al., 2019; Naeem et al., 2024; Russo et al., 2021; Siracusa et al., 2008; Vieira et al., 2011; Wu et al., 2021). Polymer-based materials with low environmental impact and reduced end-of-life concerns contribute to the overall sustainability of the above-mentioned processes. In rigid and flexible packaging with food contamination, biodegradable materials, that can be disposed as compostable waste within time frames comparable to organic waste and that meet certification requirements, contribute to efficient waste management (Geyer, 2020; Peake, 2020).

Polysaccharides are abundant, sustainable and versatile biopolymers with a long tradition in industrial applications, with their structure and relevant properties reported in numerous systematic reviews (Grzybek et al., 2024; Heinze, 2015; Heinze et al., 2018; T. Liu et al., 2023; Seidi,

Arabi Shamsabadi, et al., 2022; Seidi, Yazdi, et al., 2022; Vatanpour et al., 2022). While numerous polysaccharides with different structures are available naturally, the cost-effective production of such materials at the scale and purity required for industrial applications is still challenging. Enzymatic polymerisation of sucrose has been recently proposed to generate nature-identical polysaccharides with specific linkage control and tailored properties at scale. In this paper we focus on the α -1,3-glucan and its derivatives (Behabtu & Kralj, 2020). Such a polysaccharide is a linear, semicrystalline, water insoluble and not directly melt-processable polymer, that contains α -linked glycosidic bonds as starch. An appropriate conversion of α -1,3-glucan into its ester formulations produces melt-processable derivatives, suitable for use in many applications and processes (Adibi et al., 2022; Geitel et al., 2020; Heinze et al., 2019; Puanglek et al., 2016) such as barrier films and membrane-based separation of fluid mixtures (Bernardo et al., 2009; Drioli et al., 2021; Naeem et al., 2024; Nunes et al., 2020; Vane, 2016).

While mechanical and thermal properties for derivatives of α -1,3-

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glucan become available (Geitel et al., 2020; Kim et al., 2023; Puanglek et al., 2017), transport properties of small molecules in these materials are yet underexplored. Indeed, the practical utilisation of glucan-based materials in industrially relevant applications requires the precise determination of the transport properties of penetrants such as water and gases in relevant operative conditions. The knowledge of relationship between materials properties and their structure is required to guide future design for other and more demanding applications. There exist general correlations, often empirical, which have been provided for numerous polymers to correlate gas and water transport to their structure (Grzybek et al., 2024; Robeson et al., 2009; Smith et al., 2015). Several relevant correlations have been observed in relation to short-chain derivatives of cellulose, with gas and water sorption and transport reported for cellulose acetate (CA), cellulose propionate (CPr), and cellulose butyrate (CBu) at different Degrees of Substitution (DoS) (Chalykh et al., 2021; Chen et al., 2014; Ong et al., 2013; Puleo et al., 1989; Ricci et al., 2021). Replacing hydroxyl groups with bulkier acetyl, propionyl, or butyryl groups led to the decrease in water sorption. At the same time, the presence of bulkier groups was shown to reduce the extent of hydrogen bonding in the structure, leading to the decrease in film density and increase in water and gas permeabilities, which could be attributed to the increase in penetrant's diffusivity. The observations made on short-chain derivatives, however, cannot be directly compared to the case of long-chain derivatives of α -1,3-glucan explored here. The fibres of the unmodified α -1,3-glucan were found to offer moisture uptake nearly double that of cellulose fibres, offering an enhanced moisture management (Behabtu & Kralj, 2020). Additionally, α -1,3-glucan was successfully used as coating to improve the barrier properties of paper to water and oxygen (Adibi et al., 2022; Mishra & Dennes, 2018). The application of protective layer based on unmodified glucan and natural rubber latex allowed to decrease water absorption up to 18 times, compared to the uncoated paper (Adibi et al., 2022). Given that esterification is known to decrease water uptake in other polysaccharides, enhanced water barrier properties are expected from derivatives of α -1,3-glucan. In addition, understanding how glucan-based materials behave against other gases in terms of permeability may further allow to position them with respect to other biopolymers and synthetic polymers, such as PLA and PET.

Hence, H_2O , CO_2 , and O_2 sorption, diffusion, and ultimately their permeability and permselectivity in glucan-based materials are target properties investigated here to assess their potential in membrane separation applications, whereas understanding how structure of glucan derivatives is related to these properties is the objective of the present work. In particular, we aim to answer the following research questions: what is the extent of water uptake suppression in esters of α -1,3-glucan and how length of side-chain and its DoS affect this behaviour; what are the main structural and thermodynamic parameters governing the CO_2/O_2 performance in these materials; can a single structural parameter offer a simplified but useful tool to describe the equilibrium water sorption in glucan-based and cellulose-based materials, including mixed esters?

To answer these questions, we tested the transport properties, such as solubility, diffusivity, permeability, and permselectivity, of H_2O , CO_2 and O_2 in different self-standing films α -1,3-glucan and its esters of for the first time in the present work. Transparent films were produced by solvent casting, using two different solvents: chloroform ($CHCl_3$) and a less toxic alternative, dimethyl carbonate (DMC). We tested CO_2 and O_2 sorption, diffusion and permeation at 30 °C through a closed volume manometric device, and water vapour sorption from 0 to 100% relative humidity (RH) through gravimetric analysis at 30 °C. Furthermore, we conducted gravimetric tests with liquid water, as well as contact angle measurements to assess the wettability variations with structure. The data allowed to draw the first known quantitative correlation between water sorption properties in these materials and their structure, linking water uptake suppression to the length and the DoS of chain substituents. Moreover, we were able to confirm that different structural

aspects govern water and gas uptake in glucan esters, where the DoS of the long-chain substituent has a major effect on water sorption while the length of such substituent affects directly CO_2 and O_2 solubility. Additionally, we evaluated the effect of the solvent on transport properties, with the aim of selecting the least toxic one while maintaining the properties of the films. Finally, we provided a comprehensive comparison of the performance of glucan-based materials assessed in this work with other relevant polymers, such as cellulose-based materials, several common bio-polymers, and synthetic polymers, identifying promising applications in the membrane-separation field and providing a first tool for the structure-property correlation prediction in two classes of polysaccharides.

This study highlights the potential of glucan derivatives in practical applications and sets a reference point for future enhancements in the barrier and separation efficacy of synthetic polysaccharides, aimed at applications in barrier films or membrane separation with a low environmental footprint.

2. Experimental methods

2.1. Materials

Poly α -1,3-glucan used in this work, as well as its derivatives, is fabricated through enzymatic polymerisation of sucrose and provided by IFF Health & Biosciences. Poly α -1,3-glucan was provided as a self-standing film, while derivatives of α -1,3-glucan were provided in powder form with purities $\geq 99\%$ (assuming no moisture in the product) and used as received.

The weight average degree of polymerisation, DPw, of poly α -1,3-glucan was measured by HPLC system (Alliance™ 2695 HPLC, Waters Corporation, Milford, Mass.) equipped with a differential refractometer detector operating at 50 °C, with Dimethylacetamide (DMAc) containing 0.11 wt% Lithium Chloride (LiCl) used as mobile phase. The polymer molecular weight distribution of the glucan polymer sample was determined by comparison of retention time to a broad glucan standard. The DPw was found to be equal to 714, corresponding to 116,000 g/mol (Caimi et al., 2015). The derivatives of α -1,3-glucan, such as acetates and esters, are obtained through hydroxyl groups esterification with carboxylic acids, according to a typical procedure reported elsewhere (Behabtu & Kralj, 2020; Geitel et al., 2020; Heinze et al., 2019; Kasat & Paullin, 2016; Puanglek et al., 2016). A total of three esters of α -1,3-glucan, namely two glucan palmitates (GP1, GP2) with 1.60 and 2.30 degrees of substitution (DoS), and glucan laurate acetate (GLA), a mixed ester with 2.64 DoS for the acetyl group and 0.32 DoS for the lauryl group, were analysed and used to fabricate free-standing films via solvent casting. The reagents used for DPw analysis, DMAc and LiCl, together with the solvents used for membrane production, Chloroform ($CHCl_3$, boiling temperature, $T_b = 61$ °C) and Dimethyl Carbonate (DMC, $T_b = 90$ °C), were purchased from Merck (Darmstadt, Germany) with purities $\geq 99.0\%$ and used as received. The DPw of GP1, GP2, and GLA were determined as for poly α -1,3-glucan, and are equal to 323,000 g/mol, 456,000 g/mol, and 253,000 g/mol respectively.

The NMR spectroscopy was used to analyse the structure of glucan derivatives. The ^1H and ^{13}C NMR spectra of α -1,3-glucan were recorded on a Bruker Neo 500 MHz spectrometer (Bruker, US), using dimethyl sulfoxide- d_6 (DMSO- d_6) with 1 wt% LiCl as solvent, while deuterated chloroform ($CDCl_3$) was used for glucan esters. The signals of exchangeable protons were shifted from the anhydroglucose units (AGU) region by adding two drops of trifluoroacetic acid (TFA) to samples of glucan esters before performing ^1H analysis, used to determine DoS of substituents. In all cases the acquisition temperature was set at 40 °C. 16 and 512 scans were collected for ^1H and for ^{13}C NMR spectra respectively, with 30-degree pulse and 1 s relaxation delay. DMSO- d_6 , LiCl, $CDCl_3$, and TFA were purchased from Merck (Darmstadt, Germany) with purities $\geq 99.0\%$ and used as received.

Table 1 provides information on chemical structure, type of

Table 1Chemical structure, type of substituent (R), with DoS included in brackets, for α -1,3-glucan and its derivatives investigated in the present work.

	α -1,3-glucan	Glucan Laurate Acetate (GLA)	Glucan Palmitate (GP1)	Glucan Palmitate (GP2)
Chemical structure				
R (DoS)	Unsubstituted (0.00)	-C ₁₁ H ₂₃ (0.32) -CH ₃ (2.64)	-C ₁₅ H ₃₁ (1.60)	-C ₁₅ H ₃₁ (2.30)

substituent (R), and DoS, of α -1,3-glucan and its esters, investigated in this work, while Section S1 of the Supporting Information provides the NMR spectra for each material, together with peak assignment and integration values used to calculate the DoS (Table S1).

Deionised water (H₂O) was used for liquid and vapour sorption tests. CO₂ and O₂, used for gas sorption tests, and N₂, used as a carrier in the water vapour sorption tests, were purchased from BOC Gas & Gear (Edinburgh, UK) as specialty grade gas cylinders (CP grade) with guaranteed minimum purities $\geq 99.995\%$.

2.2. Sample preparation

The film of α -1,3-glucan provided by IFF was used as received and had a thickness of ~ 60 μm . Typically, these films are prepared by dissolving the polymer in sodium hydroxide, followed by coagulation in acid media (e.g., sulfuric acid). To maintain flexibility, films of α -1,3-glucan are soaked in a water/glycerol bath, introducing a certain amount of plasticizer in the material, that impacts both mechanical as well as barrier properties.

Self-standing films of GLA, GP1, GP2 were prepared by solvent casting. Chloroform (CHCl₃) is known to dissolve well esters of different polysaccharides and was used to form films of α -1,3-glucan derivatives, without a subsequent use of a plasticizer. The less toxic dimethyl carbonate (DMC) was also used for membrane fabrication: the solubility of these polymers in such solvent was previously unknown. It was found that only GLA can be dissolved in DMC, while all the tested glucan esters are soluble in chloroform. The polymer solutions formed by GLA, GP1 and GP2 in CHCl₃ (3 wt%, 5 wt% and 5 wt% respectively), and by GLA in DMC (3.5 wt%), were prepared and magnetically stirred at 70 °C, 40 °C, 40 °C, and 50 °C respectively until the complete solubilization of the polymer. Each solution was poured into a glass Petri dish ($\varnothing$ 60 mm) and left to evaporate on a levelled surface at room temperature (approximately 20 °C) for CHCl₃ and at 30 °C for DMC. The Petri dish was covered with a glass funnel to limit the rate of solvent evaporation and prevent contamination. A total of two membrane samples was prepared per material. The samples will be referred in the following as GLA/CHCl₃, GLA/DMC, GP1/CHCl₃, and GP2/CHCl₃. The thickness of each film, l , was measured using the Mitutoyo micrometer, with average

Table 2

Equilibrium contact angle, θ_0 , density, ρ_{pol} , and thickness, l , values for α -1,3-glucan and its derivatives investigated in the present work. Measurement uncertainty for θ_0 and l is reported as standard error, accounting for measurement variability across one and two independently cast films respectively. The uncertainty on ρ_{pol} accounts for systematic errors as well as measurement variability on a single sample.

	α -1,3-glucan	GLA/CHCl ₃	GLA/DMC	GP1/CHCl ₃	GP2/CHCl ₃
θ_0 [°]	39 $\pm$ 2	80 $\pm$ 1	81 $\pm$ 1	84 $\pm$ 1	87 $\pm$ 1
ρ_{pol} [g/cm ³]	1.11 $\pm$ 0.03	1.04 $\pm$ 0.05	1.02 $\pm$ 0.05	0.78 $\pm$ 0.02	0.87 $\pm$ 0.03
l [μm]	63 $\pm$ 8	271 $\pm$ 24	337 $\pm$ 10	322 $\pm$ 8	393 $\pm$ 4

values and standard deviations taken from 10 measurements per each material (5 per individually cast sample) and reported in Table 2 as mean and standard error, accounting for measurement variability between different films. The thickness values ranged between 270 and 390 μm , with the maximum relative error based on standard deviation equal to 8.9% for GLA/CHCl₃ samples.

Higher mixing temperature and lower concentration of GLA in CHCl₃ and DMC with respect to glucan palmitates was required to avoid gelation and obtain a low viscosity solution, suitable for a successful transfer from the vial into the Petri dish. Higher evaporation temperature is required when DMC is used as solvent, given its higher boiling point with respect to CHCl₃. All glucan ester films cast in this work were thermally treated at 40 °C under dynamic vacuum overnight to ensure the complete removal of the residual solvent prior to further characterisation.

2.3. Characterisation

2.3.1. Thermal properties

Analysis of calorimetric properties of glucan-based materials was performed using the STARE System TGA/DSC 3+ (Mettler Toledo), through thermal gravimetric analysis (TGA) and simultaneous recording of differential scanning calorimetry (DSC) heat flow measurement. Samples of about 10 mg, taken from one individually cast membrane sample per each material, were placed in an aluminium pan and were heated from 25 °C to 250 °C at 10 °C/min rate in N₂ atmosphere. All measurements were completed after performing an initial blank run, with one run recorded per sample. STARE Excellence Software was used to analyse the results.

2.3.2. Wettability

The wettability of a surface is characterised by the equilibrium or static contact angle, θ_0 , which can be defined as the angle formed at the three-phase boundary between liquid, solid, and gas, by a sessile liquid droplet on a solid surface. θ_0 for water can then range between 0° and 180° depending on the physicochemical properties of the surface, with the hydrophilicity of a solid increasing as θ_0 decreases (Law, 2014).

The equilibrium contact angle was measured for α -1,3-glucan, GLA/CHCl₃, GLA/DMC, GP1/CHCl₃, and GP2/CHCl₃ at 23 °C, ambient pressure, and ambient relative humidity, RH, of 35%. The measurements were carried out in a Drop Shape Analyser DSA30 (Krüss) by gently depositing deionised water sessile droplets with volumes ranging between 2.0 and 3.5 μL on different samples. Attention was paid to ensure that membranes were as flat as possible to avoid any effect of curvature or additional physical heterogeneities on the measurements. No major differences were observed when testing the different sides of the same sample. Schematics of the experimental setup and further details on the experimental procedure can be found elsewhere (Al Balushi et al., 2022). The data were analysed by the ADVANCE software (KRÜSS) using the ellipse (tangent 1) fitting method. Average equilibrium contact angles and standard deviations were measured using one independently cast film for each polymer, with 22 droplet depositions across the front

and back of each sample, and are reported in Table 2 as mean and standard error, accounting for variability between measurements on a single sample.

2.3.3. Liquid water sorption

Solubility and diffusivity of liquid water in α -1,3-glucan, GLA/CHCl₃, GLA/DMC, GP1/CHCl₃, and GP2/CHCl₃ were determined at 30 °C through gravimetric measurements in deionised water in a temperature-controlled water bath, according to ASTM D570 (ASTM D570-22, 2022). In terms of thermodynamic water activity, pure liquid water is equivalent to a water vapour at 100% RH.

Prior to testing, all investigated samples were conditioned at 50 °C for at least three hours in order to remove the humidity absorbed from the atmosphere. Each sample was then immersed in water for a pre-defined amount of time, periodically removed, carefully dried superficially, and weighed immediately. The procedure was repeated at different times until full saturation was reached, i.e., a time-invariant value of sample mass. The immersion time between each weighting is decided to guarantee a number of data points sufficient for characterisation, with the lowest time interval of 15 s in the initial part of the experiment and the highest time interval of 1 h after the saturation has been reached. The relative moisture uptake at time t , $m_w(t)$, is then calculated by using the following equation:

$$m_w(t) = \frac{m_s(t) - m_s(0)}{m_s(0)} \quad (1)$$

where $m_s(t)$ and $m_s(0)$ are the mass of the sample at time t and at time $t = 0$, respectively.

Water diffusion coefficient, D_w , was evaluated from the sorption transient by considering Fickian diffusion (Crank, 1979), as described in Section S3 of the Supporting Information, with an example of the sorption curve shown in Fig. S3a.

The water permeability, WP , was evaluated as the thickness-normalised mass flux of water, with water permeating through a unit area of polymer film of density ρ_{pol} and thickness l subject to a humidity difference of 100% RH:

$$WP = D_w c_w \rho_{pol} \quad (2)$$

where D_w is the average diffusivity in the 0–100% RH range measured during liquid sorption tests and c_w is the equilibrium mass liquid water concentration in the polymer. Sample densities were measured during gas sorption, as described in the gas sorption measurement section (Section 2.3.5). For each glucan derivative, 2 water sorption measurements were performed on 2 independently cast films, while for α -1,3-glucan, 4 measurements (2 per film) were conducted due to higher variability in results for this material. The values of water concentration, diffusion, and permeability, are reported as averages, with uncertainty estimated using uncertainty propagation approach (Moffat, 1988; Taylor, 1997), accounting for both systematic errors and measurement variability across different films.

2.3.4. Water vapour sorption

Water vapour solubility at 30 °C and between 0 and 95% RH in GLA/CHCl₃, GP1/CHCl₃, and GP2/CHCl₃, was determined using a gravimetric dynamic vapour sorption system (DVS, Surface Measurement Systems). Moisture uptake is determined through the difference in weight between the dry sample and the sample under a fixed given relative humidity flow by a high-precision microbalance. The water vapour/nitrogen gas mixture feeds the sample chamber at a constant flowrate. The investigated samples were conditioned in situ at 50 °C for three hours prior to testing. The sorption isotherms were obtained at a constant flow of nitrogen at 200 cm³(STP)/min by increasing the RH in the feed up to 95% in a stepwise manner. The increase in RH is performed automatically by the system after achieving equilibrium (mass variation <0.0015% s⁻¹) at each step. RH was set to 5% and 10% in the

first and second steps, then increased at intervals of 10% up to 90%, reaching 95% at the last step, for a total of 11 steps with equilibration time of 7 h each. Given the large sampling time in the DVS system, equal to 20 s, and sensors response time and volume of sampling chamber, the device is not appropriate for measuring the kinetics of water sorption. One run was recorded for GLA/CHCl₃, GP1/CHCl₃, and GP2/CHCl₃, with uncertainty on each data point evaluated based on systematic errors associated with the measurement. Each investigated sample was taken from 2 independently cast films per polymer. Further detail on the technique, system description, and uncertainty analysis can be found elsewhere (Luberti et al., 2020).

2.3.5. Gas sorption

Solubility and diffusivity of CO₂ and O₂ in esters of α -1,3-glucan, namely GLA/CHCl₃, GLA/DMC, GP1/CHCl₃, and GP2/CHCl₃, were determined at 30 °C at pressures up to 10 bar in a manometric apparatus, according to ASTM D1434 (ASTM D1434-82(2015)e1, 2015). Gas sorption was not performed on pristine α -1,3-glucan, given the presence of the plasticizer in the film, which is expected to affect gas sorption in a more drastic manner with respect to liquid sorption, thus providing results for the polymer-plasticizer mixture rather than of the pure polymer. The full equipment set-up is described elsewhere (Ferrari et al., 2010; Minelli et al., 2013; Papchenko et al., 2025). In this technique, a known amount of gas is fed into the sample cell, and the mass uptake is evaluated by measuring the gas pressure decrease over time. Sorption isotherms were obtained by performing the measurements in a step-wise manner. The density of α -1,3-glucan and its esters, ρ_{pol} , required to determine sample volume used in gas and liquid sorption tests, was obtained through helium pycnometry, i.e., by performing rapid helium expansions in the same apparatus at feed pressure lower than 1 bar, where helium solubility in the dense polymeric film is negligible (Robeson et al., 2014). Density values, reported in Table 2, are averaged from 2 measurements on a sample taken from 2 independently cast films per polymer, with uncertainty estimated through uncertainty propagation (Moffat, 1988; Taylor, 1997), taking into account systematic errors as well as variability between measurements on a single sample.

The solubility coefficient, S , is generally determined as the ratio between the equilibrium concentration of the gas in the sample, c , and the equilibrium pressure p , as follows:

$$S = \frac{c}{p} \quad (3)$$

In each sorption step, the penetrant diffusivity in the film, D , can be evaluated from the sorption kinetics (Crank, 1979), as described in Section S3 of the Supporting Information. An example of CO₂ sorption kinetics is shown in Fig. S3b.

Under the solution-diffusion framework (Wijmans & Baker, 1995; Wijmans & Baker, 2006), suitable for dense homogeneous films, the permeability coefficient of penetrant i , P_i , can be effectively evaluated as a product of its average solubility coefficient, $\bar{S}_i$, and diffusivity coefficient, D_i , in each step k :

$$P_i = \bar{S}_i D_i \quad \text{with } \bar{S}_i = \frac{c_{k+1} - c_k}{p_{k+1} - p_k} \quad (4)$$

The ideal permselectivity, α_{ij} , between gas i and j , under the assumption of negligible downstream pressure compared to upstream pressure, is the ratio between pure-gas permeabilities. As permeability, the permselectivity can also be seen as the product of solubility-selectivity, α_{ij}^S , and diffusivity-selectivity, α_{ij}^D :

$$\begin{aligned} \alpha_{ij} &= \frac{P_i}{P_j} = \frac{\bar{S}_i}{\bar{S}_j} \cdot \frac{D_i}{D_j} \\ &= \alpha_{ij}^S \cdot \alpha_{ij}^D \end{aligned} \quad (5)$$

The ideal permselectivity is generally used as a first estimate of the separation performance of new materials and its comparison with

existing literature data.

Gas permeability is typically measured in $[mol\ m/(m^2\ s\ Pa)]$ in SI system. A different unit is more widely used within membrane community, i.e., $[Barrer] = [10^{-10}\ cm^3(STP)\ cm/(cm^2\ s\ cmHg)]$. Another unit, typically used with reference to packaging materials, is $[g\ mm/(m^2\ day)]$. These units can be converted into one another as follows:

$$\begin{aligned} 1 \frac{mol\ m}{m^2\ s\ Pa} &= 2.99 \times 10^{15} Barrer \\ &= 1.56 \times 10^9 \times p_{vap}^{H_2O}(T) \frac{g\ mm}{m^2\ day} \end{aligned} \quad (6)$$

where $p_{vap}^{H_2O}(T)$ is the water vapour pressure at the temperature of the sorption experiment, in Pa.

Values of gas concentration, solubility, diffusivity, permeability, and selectivity are reported as average values from 2 measurements per each sample, taken from 2 independently cast films per polymer, with uncertainty estimated using uncertainty propagation approach (Moffat, 1988; Taylor, 1997), accounting for both systematic errors and variability between measurements on a single sample.

3. Results and discussion

3.1. Membrane appearance and characterisation

The self-standing film of α -1,3-glucan, shown in Fig. 1a, was provided by IFF Health & Biosciences and used as received. The films of three esters of α -1,3-glucan, namely GP1, GP2, and GLA, were prepared by solvent casting with two solvents considered for the membrane preparation. Chloroform was chosen as it is known to dissolve glucan-based materials (Geitel et al., 2020; Heinze et al., 2019). Dimethyl Carbonate (DMC) was selected as a greener alternative, given its lower ecotoxicity, biodegradability, lower hazard associated with handling, and previous use for membrane fabrication of biopolymers (Jessop,

2011; Papchenko et al., 2022; Pyo et al., 2017). Only GLA was found to be soluble in DMC, and samples of GLA cast from both $CHCl_3$ and DMC were considered for further characterisation. Fig. 1 shows four films of α -1,3-glucan derivatives prepared and characterised in the present work. All glucan ester samples are macroscopically homogeneous, fully transparent, and present good flexibility, with no use of a plasticizer.

The structural analysis was performed by means of ^1H and ^{13}C NMR spectroscopy, as reported in Section S1 and Fig. S1 of the Supplementary information. The spectra allow to appreciate qualitatively the relative presence of functionalised groups in each ester. The peaks of the α -1,3-glucan substrate are fully assigned in the ^{13}C spectra, with peaks at chemical shift of 60.8, 70.0, 71.5, 72.5, 82.8, and 100.1 ppm assigned to C6, C4, C2, C5, C3, and C1 respectively (Fig. S1a), in agreement with previous works (Heinze et al., 2019). Two additional peaks are visible at 63.5 and 73.1 ppm that can be attributed to glycerol, used as plasticizer for α -1,3-glucan. The spectra of glucan esters (GLA, GP1, and GP2) present $-CH_3$ peaks attributable to laurate and palmitate substituents at 14 ppm, and acetate substituents at 20 ppm, together with $C=O$ peaks in the 169 to 171 ppm region. As an example, the spectra of the most substituted glucan derivative, GLA, shows three peaks in the $C=O$ region, in line with esterification of C6-OH, C4-OH, and C2-OH groups. This is consistent with the shift of C1 peak from 100.1 to 95.0 ppm in the spectra, when compared to α -1,3-glucan, due to the presence of ester groups at the position 2, i.e., substituting the secondary hydroxyl group (C2-OH). At the same time, the peak attributable to C6 is not significantly shifted from 60.8 ppm, which indicates the presence of unreacted C6-OH primary groups in the structure. The GLA spectra in the $C=O$ region is consistent with what has been previously observed for highly substituted glucan acetates (Heinze et al., 2019). The GP1 and GP2 ^{13}C spectra showed broad peaks in the AGU region consistent with esterified product but poor signal to noise ratio, limiting the conclusions that can be drawn on the substitution pattern. In addition to ^{13}C NMR spectroscopy, ^1H spectra for the three glucan esters are shown in Figs. S1b, S1c, and S1d respectively, with peak assignment and integration used to evaluate the degree of substitution of each substituent reported in

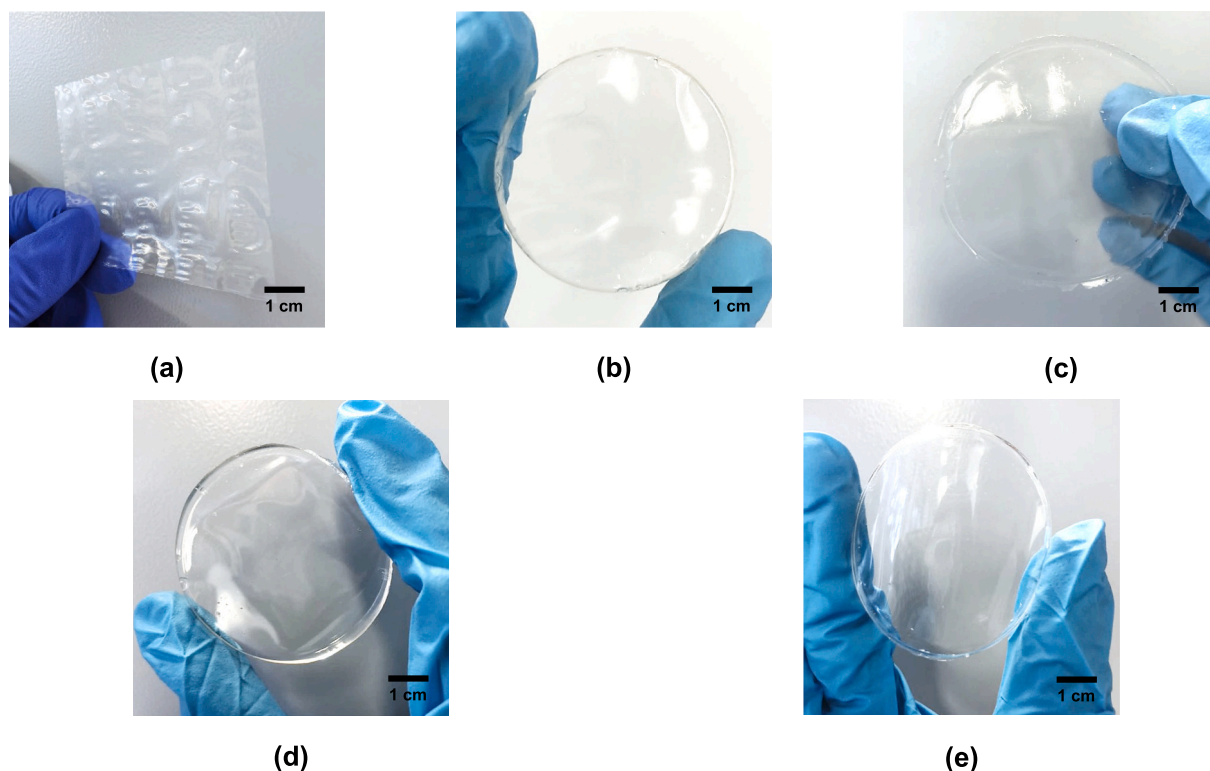


Fig. 1. Films of (a) α -1,3-glucan and its esters: (b) GLA/ $CHCl_3$, (c) GLA/DMC, (d) GP1/ $CHCl_3$, and (e) GP2/ $CHCl_3$. A total of two films were cast per each polymer.

Table S1. All spectra present peaks in the ~ 6 to ~ 3 ppm region attributable to the anhydroglucose glucan unit (AGU). The stack of ^1H spectra, reported in Fig. S1e, allows to compare the AGU region in the unsubstituted polymer and its esters. The peaks attributable to hydrogens of C2 to C6 atoms are shifted towards higher ppm in GLA due to the substantial acetylation. In case of GPs, the AGU region presents a significant level of complexity deriving from the overlap of substituted and unsubstituted peaks, which is typical of derivatised polysaccharides. The laureate and acetate $-\text{CH}_3$ peaks are assigned at 2.16 and 0.90 ppm for GLA, with intensity (and integral) of the acetate peak being much higher to reflect the higher DoS. Additional peaks between 2.19 and 1.29 ppm are attributed to laurate $-\text{CH}_2-$ groups. The palmitate $-\text{CH}_3$ peaks are assigned at 0.91 and 0.92 ppm in GP1 and GP2, respectively, while the peaks between 2.44 and 1.30 are attributed to palmitate $-\text{CH}_2-$ groups. The intensity (and integrals) of $-\text{CH}_3$ and $-\text{CH}_2-$ peaks in GP2 are higher, reflecting the higher DoS. Peak assignment is consistent with what has been previously observed for esters of α -1,3-glucan (Geitel et al., 2020). The calculated values of DoS of each glucan derivative examined in this work are reported in Table 1 (Section 2.1).

Calorimetric properties of all samples in the temperature range of application interest were analysed through TGA combined with DSC measurements, with the results shown in Section S4 (Fig. S4) of the Supporting Information. The analysis was performed between 25 °C and 250 °C to evaluate thermal transitions without reaching degradation of glucan derivatives. A 12% loss in weight was observed for α -1,3-glucan between 40 °C and 150 °C and < 5% loss in weight was found for all the other samples after reaching 200 °C (Fig. S4a). All samples showed a colour change from clear to amber after the analysis. The weight loss in α -1,3-glucan can be attributed to both the plasticizer and atmospheric moisture, where approximately 7% of mass loss occurs at temperatures up to 100 °C and can be mainly attributed to moisture. In addition, DSC analysis (Fig. S4b) showed neither melting peaks, indicating the amorphous nature of the glucan esters, nor glass transition-related peaks. Long-chain cellulose esters are known to show melting peaks that can be attributed to the side-chain crystallisation. In particular, the melting peaks related to crystallinity can be observed when DoS is low enough (< 1) allowing for more efficient side-chain organisation (Willberg-Keyriläinen et al., 2017). On the other extreme, the crystallinity is present when the side-chain length is high enough (> C12) to restrict the mobility of the cellulose backbone (Crépy et al., 2011; Sealey et al., 1996). In the case of glucan esters analysed here, where DoS is higher than 1 and the side-chain length is high (> C12 for GPs), no melting peaks were observed, which suggests amorphous structures due to poor side-chain organisation mostly due to higher DoS. Pure α -1,3-glucan is known to melt and decompose above 300 °C (Behabtu & Kralj, 2020), while thermal properties of its long-chain esters have been measured, to the best of our knowledge, only at DoS = 3 and up to side chain lengths of 8 carbon atoms, where no transition peaks were observed up to 300 °C for side chains with more than 6 carbon atoms (Puanglek et al., 2017). While not directly comparable, the results presented here are consistent with what has been observed in literature for glucan esters, however a more systematic analysis would be needed to clarify the side-chain crystallisation behaviour in these materials, which is out of scope for this work. Moreover, the membrane preparation technique used in this work could additionally restrict the efficient chain packing due to the rapid solvent casting. The absence of side-chain crystallinity in glucan esters has a direct consequence on their gas transport, with transport properties in amorphous phase being higher than in the corresponding semi-crystalline material, as gas molecules are known not to absorb or diffuse through the crystalline phase. Hence any difference in gas solubility and diffusivity observed for glucan-based and cellulose-based materials can be partially attributed to the difference in side-chain crystallinity, on top of other structural factors.

The density of all samples, evaluated by means of helium expansion as described in Section 2.3.5, is reported in Table 2. The measured density of α -1,3-glucan is lower than the backbone density of this

polymer, which is expected to be approximately 1.5 g/cm³ as in the case of cellulose (Heinze, 2015; Sun, 2008). The lower density value measured generally indicates process induced defects, that could impact the material's performance.

Next, the wettability of the membranes was evaluated via the equilibrium contact angle, θ_0 , which was measured for α -1,3-glucan and GLA/CHCl₃, GLA/DMC, GP1/CHCl₃, and GP2/CHCl₃ membranes at ambient temperature, pressure, and relative humidity (23 °C, 35% RH), as described in Section 2.3.2. No major differences were observed when testing different sides of the film, suggesting that sample preparation had no effect on the physiochemical properties of the different membranes' sides. The snapshots of a droplet deposited on the tested membranes and their associated droplet shape fitting and contact angle measurements performed on each film are shown in Fig. 2 as an example. The contact angle values along with their standard errors for each sample are reported in Table 2.

The presence of different substituents at varying DoS makes it challenging to correlate the structure of glucan esters to their properties. For this reason, we introduced a specific structural parameter – the C/O functional group ratio, $R_{C/O}$, defined as the ratio between the number of functional groups containing carbon atoms and those containing oxygen atoms. The choice of carbon and oxygen is motivated by the prevalence of these atoms in the structure of all polymers studied. The calculation of $R_{C/O}$ is performed by dividing the monomer into structural groups, similarly to the approach used in group contribution methods. The total number of functional groups containing carbon atoms is then counted and divided by the number of functional groups containing oxygen. Table 3 reports the functional group count for monomers of polymers investigated here, together with values of the C/O functional group ratio. Taking GLA as an example, its monomer presents on average 5 $>\text{CH}-$ groups in the ring, 4.2 $-\text{CH}_2-$ groups, of which 1 belongs to the ring and 3.2 to the lateral chain (calculated as 10(C in lauryl group)*DoS (lauryl group)), 2.96 $-\text{CH}_3$ and 2.96 $-\text{COO}-$ groups, of which 0.32 belong to the lauryl group and 2.64 to the acetyl group, for a total number of 4 functional groups containing carbon. Moreover, $-\text{COO}-$ groups are also accounted for as containing oxygen atom, together with 2 $-\text{O}-$ groups, in the ring and connecting the rings, and only 0.04 $-\text{OH}$ groups, calculated subtracting DoS(lauryl group) and DoS(acetyl group) from the maximum DoS available for α -1,3-glucan (i.e., 3). Thus, summing all the contributions, $R_{C/O} = \frac{15.1}{5.0} = 3.0$ for GLA.

The equilibrium contact angle increases with increasing $R_{C/O}$ and DoS of the long-chain substituent (Pasquini et al., 2006; Sheppard & Newsome, 1935). In particular, θ_0 is equal to 39° for α -1,3-glucan, to 80° and 81° for GLA/CHCl₃ and GLA/DMC respectively, to 84° for GP1/CHCl₃ and 87° for GP2/CHCl₃, as shown in Fig. 3a. The contact angle increases more gradually and regularly with the parameter $R_{C/O}$ than with DoS. This is because the esterification of α -1,3-glucan reduces the amount of hydroxyl groups in the structure, and thus a decrease in hydrophilicity is expected with increasing DoS. If the substituent is hydrophobic, an additional depression in hydrophilicity with increasing chain length of the substituent should be observed, quantified by $R_{C/O}$.

A similar trend has been reported for β -1,4-glucan (cellulose): the contact angle increases from 30° in cellulose to 76° and 79° in cellulose caprylate and cellulose laurate, respectively, at low values of DoS, reaching values of 99° and 101° when high DoS are considered (Pasquini et al., 2006; Sheppard & Newsome, 1935). Overall, the esterification of α -1,3-glucan with long-chain fatty acids increases the contact angle by over 100% on average.

3.2. Water sorption and transport

Water uptake and permeability suppression by esterification is a known approach for polysaccharides to impart water barrier properties desirable for industrial applications. Here, we assess the extent of water transport properties variation in glucan-based polymers through

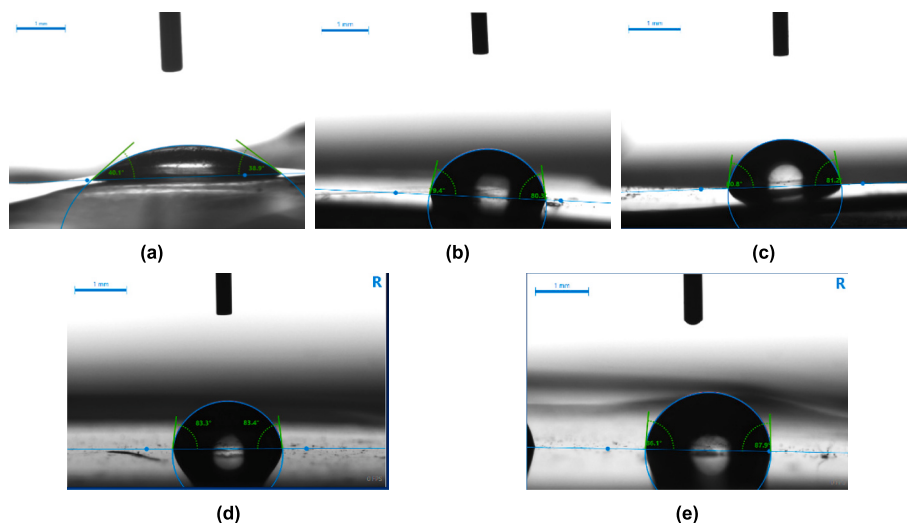


Fig. 2. Snapshots of equilibrium contact angle, θ_0 , measurements in α -1,3-glucan and its esters: (a) α -1,3-glucan, (b) GLA/ CHCl_3 , (c) GLA/DMC, (d) GP1/ CHCl_3 , (e) GP2/ CHCl_3 . The measurements were performed using one individually cast film per polymer.

Table 3

Parameters for calculation of $R_{C/O}$ for glucan-based materials investigated in this work.

Group	Structural group count			
	α -1,3-glucan	GLA	GP1	GP2
$-\text{CH}_2-$	1	4.2	23.4	33.2
$>\text{CH}-$	5	5	5	5
$-\text{O}-$	2	2	2	2
$-\text{OH}$	3	0.04	1.40	0.70
$-\text{COO}-$	0	2.96	1.60	2.30
$-\text{CH}_3$	0	2.96	1.60	2.30
Ring	1	1	1	1
$R_{C/O}$	1.2	3.0	6.3	8.6

gravimetric measurements in deionised water (100% RH) at 30 °C, as described in Section 2.3.3, and by measurements in the vapour phase (Section 2.3.4) for RH values ranging from 0% to 95% for GLA, GP1, and GP2 cast from CHCl_3 in a DVS system at the same temperature.

Given the structural similarity of α -1,3-glucan and β -1,4-glucan (Behabtu & Kralj, 2020), it is reasonable to expect similar behaviour in terms of water solubility and transport in these polymers. While both polysaccharides are insoluble in water, the moisture uptake at 65% RH of α -1,3-glucan-based fibres was found to be $\sim$ 23% and almost double that of cellulose-based fibres (Behabtu & Kralj, 2020). At the same time, equilibrium water concentration in cellulose can reach up to 40% in weight at higher values of RH, as reported in literature (Aulin et al., 2010; Chalykh et al., 2021; Meriçer et al., 2017; Simon et al., 2022). Such a high value of water solubility can be attributed mainly to the presence of hydroxyl groups in the polymeric structure, that act like water sorption sites and are responsible for hydrophilic behaviour. Acetylation and esterification reduce the amount of hydroxyl groups while introducing carbonyl oxygens, both available for water sorption, overall improving cellulose and α -1,3-glucan barrier properties towards water. Indeed, water solubility in cellulose acetates was found to decrease with increasing degree of substitution (Chalykh et al., 2021; Simon et al., 2022). Similar water sorption behaviour is observed in the present work for the α -1,3-glucan derivatives.

The equilibrium liquid water uptake, c_w , for α -1,3-glucan and films of GLA/ CHCl_3 , GP1/ CHCl_3 , and GP2/ CHCl_3 , is shown as a function of $R_{C/O}$ in Fig. 3b. $R_{C/O}$ is chosen, rather than DoS, to better reflect the presence of a mixed ester in the analysed polymers. As reported in Table 3, the $R_{C/O}$ increases with increasing DoS of the long-chain

substituent in this work, thus the trends observed with $R_{C/O}$ are consistent with those related to DoS. As expected from wettability measurements, water solubility decreases with increasing $R_{C/O}$ in esters of α -1,3-glucan, and the trend is opposite to that of the equilibrium contact angle, shown in Fig. 3a. The water uptake in the film of α -1,3-glucan was found to be 53% at 100% RH, which is 30% higher than that of cellulose in a similar condition ($\sim$ 40% in weight (Chalykh et al., 2021; Meriçer et al., 2017; Simon et al., 2022)). The difference observed between the two unsubstituted polysaccharides can be mainly attributed to the difference in the backbone type, as this has a direct repercussion on the chain conformation and the amount of hydroxyl groups available for interaction. While the structural conformation of the two polymers was found to be similar (Behabtu & Kralj, 2020), the primary hydroxyl groups, or hydroxymethyl groups, seem to be more exposed to interactions in case of α -1,3-glucan (Ogawa et al., 1981; Wohler et al., 2022). As water interaction with primary hydroxyl groups is favoured over secondary ones, due to energetic factors as well as steric hindrance (Nilsson et al., 2023), it can be argued that structural differences and higher wettability are the main reason for higher water uptake in α -1,3-glucan. The difference in water uptake, however, is minor when compared to the substantial variability seen in the substituted polysaccharides, where water uptake ranges across three to four orders of magnitude and is highly dependent on the substituent, as further quantified in Section 3.6.

The presence of a linear aliphatic chain as substituent in glucan esters allowed to substantially decrease α -1,3-glucan water uptake by up to two orders of magnitude, with values ranging from $\sim$ 3 to 0.5% in weight. In particular, the water uptake was 18, 40, and 97 times lower in GLA, GP1, and GP2, with respect to the unmodified polymer. The reduction in water solubility can be attributed directly to the decrease in the amount of water absorption sites and to the lower wettability of the membranes upon esterification, which in addition leads to the reduction of the plasticising effect of water in glucan esters with respect to the neat glucan. Fig. 3b allows to appreciate the non-linearity of the esterification effect on water uptake: increasing the $R_{C/O}$ from 1.2 to 3.0 in GLA decreased the equilibrium water concentration by a factor of 18, while further increasing the $R_{C/O}$ to 8.6 in GP2 led to an additional fivefold decrease in water uptake. If this trend is conserved, mass water uptake in the range of 0.1% at 100% RH can be expected from a fully substituted α -1,3-glucan, with length of substituent similar to the esters investigated here. The correlation of contact angle and water uptake with $R_{C/O}$ shown here allows to establish a significant structure-property relationship in these materials.

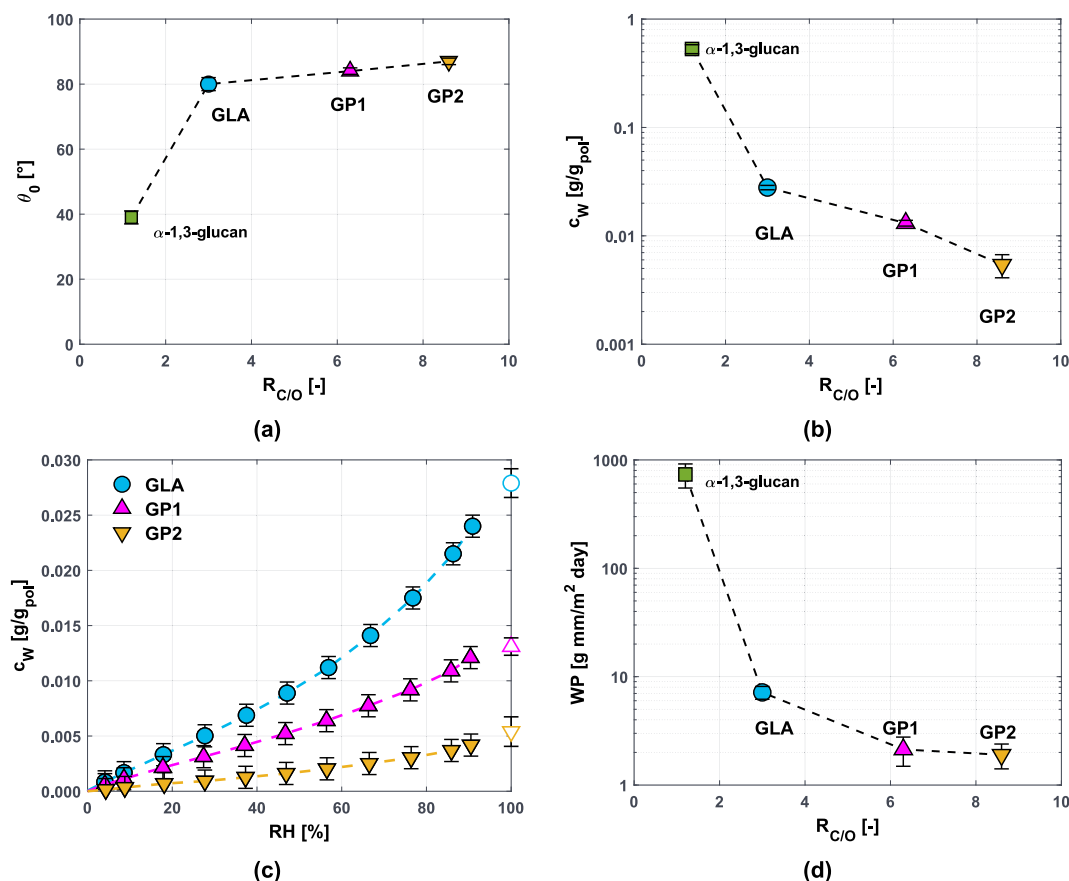


Fig. 3. Wettability and water transport properties at 30 °C in films of α -1,3-glucan and its esters, cast from CHCl_3 . (a) Equilibrium contact angle θ_0 at 23 °C and 35% RH (uncertainty reported as standard error from up to 22 measurements on one independently cast film per polymer) and (b) Equilibrium water uptake as function of $R_{C/O}$ (uncertainty represents measurement variability across 2 films per each polymer). (c) Water sorption isotherms for 0 to 100% RH, from DVS (filled symbols) (uncertainty given by systematic errors associated with the measurement) and from liquid water sorption (empty symbols) measurements. (d) Water Permeability, WP, calculated according to Eq. 3, as function of $R_{C/O}$. Dashed lines are reported to illustrate the trend.

The water vapour sorption isotherms for GLA, GP1, and GP2 samples cast from CHCl_3 at values of RH ranging from 0% to 100% are shown in Fig. 3c. All three materials present isotherms similar in shape to those of cellulose esters (Chalykh et al., 2021). Water vapour solubility is found to decrease with $R_{C/O}$ at all values of RH. Glucan ester with the lowest DoS of the long-chain substituent, GLA, presents the highest deviation from linearity with increasing RH. This deviation from linearity can be attributed to a higher plasticising effect exerted by water on GLA with respect to the more hydrophobic GP1 and GP2 due mainly to the structural difference. It is noteworthy that the water vapour uptake determined via DVS is in excellent agreement with values obtained via liquid water sorption at 100% RH, which thus represents the upper boundary for water solubility in the materials investigated.

The increase in DoS and in length of the long-chain substituent, which leads to increased $R_{C/O}$, plays a major role in water sorption, similarly to what has been observed for cellulose esters (Chalykh et al., 2021; Simon et al., 2022). The presence of functional groups able to interact with water molecules and their accessibility are the main factors influencing the equilibrium water uptake in polymeric materials, and are the direct consequence of structural conformation. As in the case of unsubstituted polymers, water is expected to mostly interact with hydroxyl and $-\text{COO}-$ groups introduced through esterification, while oxygen atoms in the pyranose ring and in the glycosidic linkage are somewhat shielded due to steric effects. Molecular dynamics simulations can be used to analyse the strength of water interactions with functional groups, and this has been done in case of cellulose esters (Nilsson et al., 2023). In their work, water was shown to preferentially interact with the carbonyl oxygen of ester groups over hydroxyl groups. Moreover, as the

carbonyl oxygen is more exposed to water molecules when a shorter alkyl chain is attached to the backbone, the interaction was found to be stronger for acetyl groups. This is consistent with experimental observations reported here: GLA is the most substituted ester mainly with acetyl groups in the structure, which justifies its higher water uptake when compared to GP1 and GP2. Moreover, the presence of long aliphatic chains in all glucan derivatives investigated here reduces the fraction of hydroxyl and ester groups available for interaction with water over the total number of functional groups present in the polymer. It introduces additional steric effects that reduce accessibility to both hydroxyl and ester groups. This translates in water uptake being the lowest in the ester with highest DoS of the long-chain substituent and the longest side chain, GP2. Finally, even longer side chains with respect to those analysed here might crystallise, as happens in cellulose-based materials (Crépy et al., 2011; Sealey et al., 1996), which would further reduce water uptake. Overall, the number of functional groups in the structure of the same polymeric class emerges as the dominant parameter to be used for water sorption correlation in modified polymers, as it dictates the availability of interaction sites, steric hindrance, and potential presence of crystalline domains. Variation in DoS or in length of substituents contributes differently to the function group count, and both effects can be consistently accounted for by using a more general structural parameter like $R_{C/O}$. The results obtained for glucan-based materials in terms of water uptake suppression can then be further generalised to other polysaccharide esters based on their $R_{C/O}$, as long as the functional groups in the backbone are similar. A more detailed comparison with the performance of cellulose-based materials would be

needed to quantify the backbone modification effect on water uptake and to compare it to the esterification effect, and it is reported further, in Section 3.6. The strength of water and other penetrants' interaction with functional groups, however, is better described by thermodynamics parameters, and relevant discussion is further provided in Section 3.4.

Water diffusion coefficients, calculated from sorption transient at 100% RH and reported in Table 5 (Section 3.6), showed a less clear trend with $R_{C/O}$. The diffusion value of 1.5×10^{-7} cm²/s for α -1,3-glucan decreases by a factor of 5, down to 2.9×10^{-8} cm²/s, upon substitution with lauric acid and acetic acid in GLA. For the glucan palmitate with the lower DoS (GP1) the water diffusion coefficient is similar to GLA (2.4×10^{-8} cm²/s), but it doubles by further increasing the DoS to 2.30, with

GP2 showing a value of 4.7×10^{-8} cm²/s. Finally, water permeability at 100% RH, WP , was evaluated as the product of solubility and diffusivity, with values decreasing with $R_{C/O}$, as shown in Fig. 3d. Esterification of α -1,3-glucan led to a significant decrease of water permeability, with GP2 reaching a value 400 times lower compared to the unmodified glucan. Assuming a similar trend is conserved at higher DoS and $R_{C/O}$, WP in the range of 1 g mm/(m² d) at 100% RH can be expected from fully substituted α -1,3-glucan, with substituent lengths similar to the esters investigated here.

The water solubility and transport analysis presented here clarifies how the length of the side chain and its DoS, effectively described by $R_{C/O}$, affect their water barrier performance in esters of α -1,3-glucan by

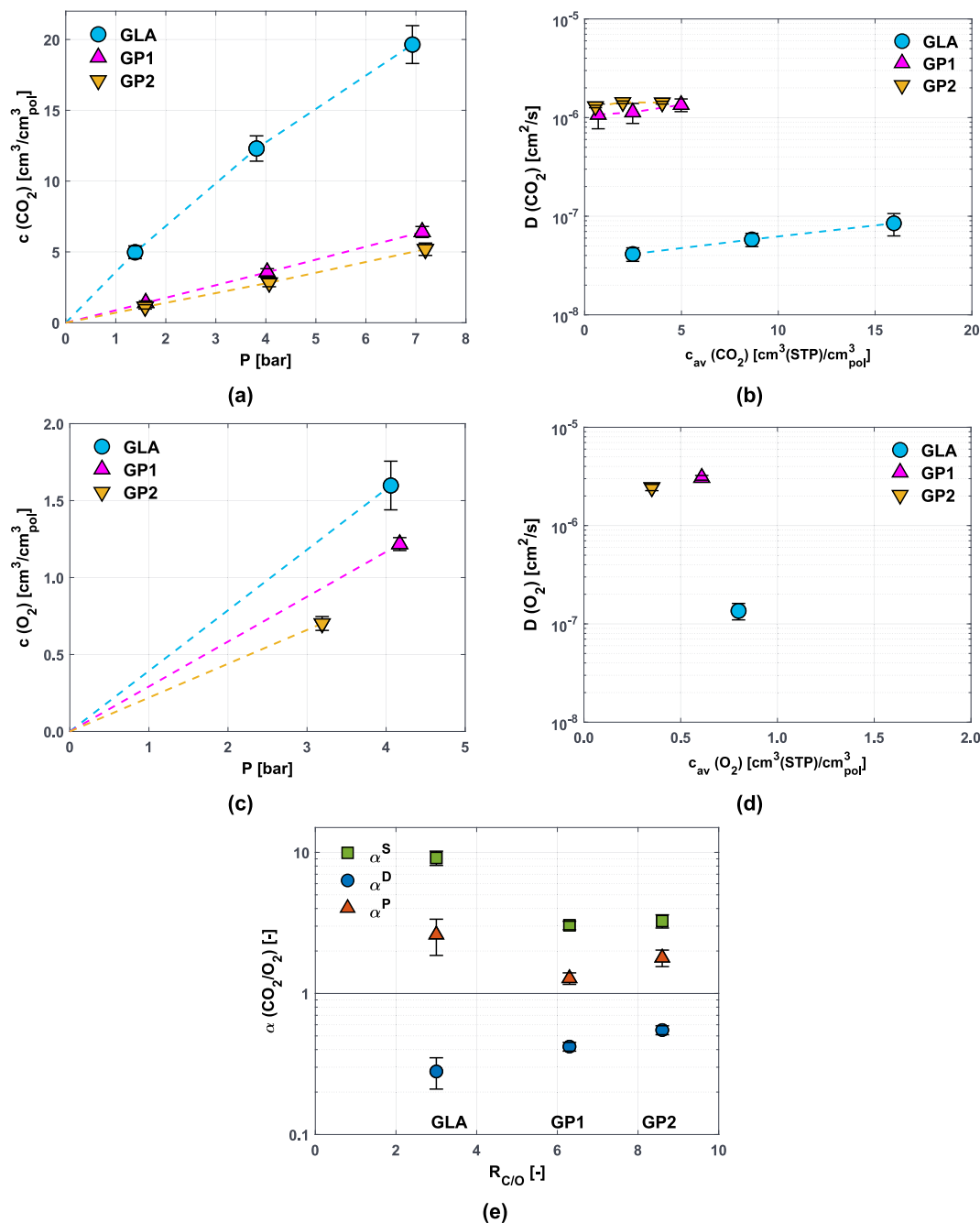


Fig. 4. Gas transport properties at 30 °C in esters of α -1,3-glucan, cast from Chloroform, GLA, GP1, and GP2, investigated in this work: (a) CO₂ and (c) O₂ sorption isotherms as c function of P ; CO₂ and O₂ diffusion coefficients as function of average (b) CO₂ and (d) O₂ concentration; (e) CO₂/O₂ solubility, diffusivity, and permselectivity, α^S , α^D , and α^P , as function of $R_{C/O}$ in GLA, GP1, and GP2. The reported uncertainties account for systematic errors as well as for measurement variability on a sample taken from 2 individually cast films per polymer.

changing the type, number, and accessibility of functional groups able to interact with water molecules in the polymeric structure: the liquid water uptake in grams of water per grams of polymer decreased by ~ 100 times in the highly substituted glucan palmitate with respect to unmodified glucan, while permeability was found to be ~ 400 times lower in the same material. Liquid sorption analysis was also performed on GLA/DMC sample, with results reported and discussed in Sections 3.4, 3.5, and 3.6.

3.3. Gas transport

In order to evaluate the influence of structural and thermodynamic parameters on CO_2 and O_2 transport and CO_2/O_2 performance in glucan-based materials, an in-depth analysis of sorption, diffusion, permeation, and respective selectivities, is essential. To this end, the aforementioned properties were investigated in GLA/ CHCl_3 , GLA/DMC, GP1/ CHCl_3 , and GP2/ CHCl_3 at 30°C and at pressures up to 10 bar by the pressure decay apparatus, with results reported in Fig. 4 and Table 5 (Section 3.6). As discussed in Section 2.3.5, gas sorption was not performed on the film of unmodified α -1,3-glucan, as gas transport properties are expected to be highly impacted by the presence of the plasticizer in the structure thus the values would not be truly representative of this polymer. An example of CO_2 sorption kinetics and the fitting of its transient behaviour are shown in Fig. S3b. The behaviour is qualitatively similar to that of liquid water, although the tests are performed with different methodologies.

Fig. 4a presents CO_2 sorption isotherms, with CO_2 concentration reported as function of pressure, in GLA, GP1, and GP2, cast from CHCl_3 . It is noteworthy that CO_2 concentration at different pressures follows the same trend with hydrophilicity observed for water sorption in these materials, which also relates as $S_{\text{CO}_2}(\text{GLA}) > S_{\text{CO}_2}(\text{GP1}) > S_{\text{CO}_2}(\text{GP2})$. In particular, CO_2 solubility evaluated in GLA, $S_{\text{CO}_2}(\text{GLA})$, at the equilibrium pressure of 1 bar (Table 5) is 4 and 5 times higher than $S_{\text{CO}_2}(\text{GP1})$ and $S_{\text{CO}_2}(\text{GP2})$ respectively. Such behaviour could be attributed to the fact that CO_2 has a quadrupolar moment and the polarity of the polymer favours the gas-polymer interactions. However, while water solubility is highly dependent on the $R_{\text{C/O}}$ and DoS, the CO_2 solubility seems to be mostly affected by the chain length of the substituent, as the solubility of GP1 and GP2, which differ only by DoS, is very similar. The solubility of O_2 follows a similar trend to H_2O and CO_2 , as shown in Fig. 4c and Table 5, with O_2 solubility in GLA being 1.3 higher than in GP1 and 1.8 times higher than in GP2.

The shape of CO_2 isotherm in GLA is slightly concave to the pressure axis, which is generally associated with glassy polymers, while GP1 and GP2 present linear isotherms for CO_2 , due to the lower solubility in these polymers and onset of a Henry's law type of mechanism (Matteucci et al., 2006), which is associated to rubbery polymers. O_2 isotherms were found to be linear with pressure for all three polymers at the same testing conditions. As discussed in Section 3.1, no relevant thermal transitions were observed during DSC analysis (Section S4 of the SI), suggesting the amorphous nature of glucan esters, but with no indication of their behaviour with respect to glass transition. Previous studies showed a significant depression in glass transition temperature with increasing side chain length of fatty acid groups in fully substituted glucan esters, with values ranging from 168°C for α -1,3-glucan acetate (DoS = 3) to 16°C for α -1,3-glucan octanoate (DoS = 3) (Puanglek et al., 2017). This is in agreement with the gas sorption behaviour reported here, as the CO_2 isotherm shape is consistent with the assumption of glassy nature of GLA and rubbery nature of GPs at 30°C . This indirect interpretation, based solely on sorption data, requires confirmation by direct thermal techniques, such as dynamic mechanical or dielectric analysis, to determine the actual glass transition temperature of these samples at their given DoS.

Fig. 4b shows CO_2 diffusivity, evaluated from the sorption transient, at different average concentrations of the gas. The CO_2 diffusion coefficient in GP1 and GP2 is rather high ($10^{-6} \text{ cm}^2/\text{s}$), and it is more than an

order of magnitude lower in GLA at the same average concentration of the gas. A similar trend is observed for O_2 , which shows higher diffusion coefficients with respect to CO_2 (Fig. 4d). Both CO_2 and O_2 diffusivity values in glucan palmitates are comparable to those of unvulcanised natural rubber, an amorphous analogue of polyethylene, suggesting that gas transport in these materials is largely dominated by the presence of an aliphatic side chain (Michaels & Bixler, 1961).

The much higher diffusivity of CO_2 in glucan palmitates compared to GLA, as reported in Fig. 4b, leads to its lower permeability in the mixed ester, with $P_{\text{CO}_2}(\text{GP1}) > P_{\text{CO}_2}(\text{GP2}) > P_{\text{CO}_2}(\text{GLA})$ as it is later conveyed in Section 3.4 and shown in Fig. 5b. The same was found to be true for O_2 permeability. Cellulose esters present a relatively similar behaviour, where CO_2 and O_2 permeability were found to increase mainly with increasing length of the side-chain (Chen et al., 2014; Willberg-Keyriläinen et al., 2017).

Finally, the ideal CO_2/O_2 permselectivity, α^P , (Fig. 4e) can be evaluated at 1 bar as the product of solubility- (α^S) and diffusivity- (α^D) selectivity and correlated to the $R_{\text{C/O}}$ of esters of α -1,3-glucan. It is interesting to notice how all three materials present CO_2/O_2 diffusivity-selectivity lower than unity, similarly to semicrystalline polyethylene and its amorphous analogue (Michaels & Bixler, 1961), which is increasing with $R_{\text{C/O}}$. The solubility-selectivity, on the other hand, reaches a value of ~ 10 in GLA and decreases to a value of ~ 3 in both GP1 and GP2. The product of thermodynamic and kinetic factors leads to values of ideal CO_2/O_2 permselectivity higher than unity but with no particular trend with $R_{\text{C/O}}$.

The analysis of CO_2 and O_2 transport properties in esters of α -1,3-glucan allows to conclude that the main structural parameters governing the CO_2 and O_2 sorption and transport in glucan-based materials are the type and length of the side chain rather than the DoS: the CO_2 solubility in GPs is very similar despite the difference in DoS, while the side-chain aliphatic nature affects directly CO_2 and O_2 diffusion and diffusivity-selectivity in GP2, resulting in values comparable to those of an amorphous analogue of polyethylene. Moreover, these materials are overall CO_2 -selective and present values of CO_2 permeability that range over an order of magnitude. Additionally, given quite high values of CO_2 permeability in GP1 and GP2 ($> 100 \text{ Barrer} = 3.34 \times 10^{-14} \text{ mol m}/(\text{m}^2 \text{ s Pa})$), these materials could be investigated for gas membrane separations of industrial relevance, where CO_2 needs to be removed from other gases, and the assessment of their suitability for these applications should be an object of study for future work. A more detailed comparison of CO_2/O_2 separation properties with cellulose esters and other polymers is reported in Section 3.6, while analysis of GLA/DMC sample is reported and discussed in Sections 3.4, 3.5, and 3.6.

3.4. Influence of penetrant and polymer properties on penetrant transport

Fig. 5 allows to examine how solubility and permeability of H_2O , CO_2 , and O_2 depend on the properties of pure penetrants in esters of α -1,3-glucan, examined in the present work.

Penetrant solubility is generally correlated to its critical temperature, T_c , which gives a measure of the penetrant condensability, while the diffusion coefficient is usually related to its kinetic diameter, d_k , which reflects the molecular dimension of the penetrant (Matteucci et al., 2006). The solubility of the three penetrants, S , shown in Fig. 5a, increases regularly with their critical temperature in GLA, GP1, and GP2, as expected (Matteucci et al., 2006), with $S_{\text{H}_2\text{O}} > S_{\text{CO}_2} > S_{\text{O}_2}$. The diffusivity, D , however, seems to increase with the penetrant size, as reported in Table 5 (Section 3.6), contrarily to the generally observed behaviour for polymeric materials (Matteucci et al., 2006). Such behaviour could be attributed to the importance of interactions between penetrant and polymer, which are related to solubility, that might reduce molecule's mobility in the polymeric matrix (Ghosal et al., 1996; Papchenko et al., 2023). The permeability values, P , of the three penetrants, taken as product of their solubility and diffusivity, correlate quite

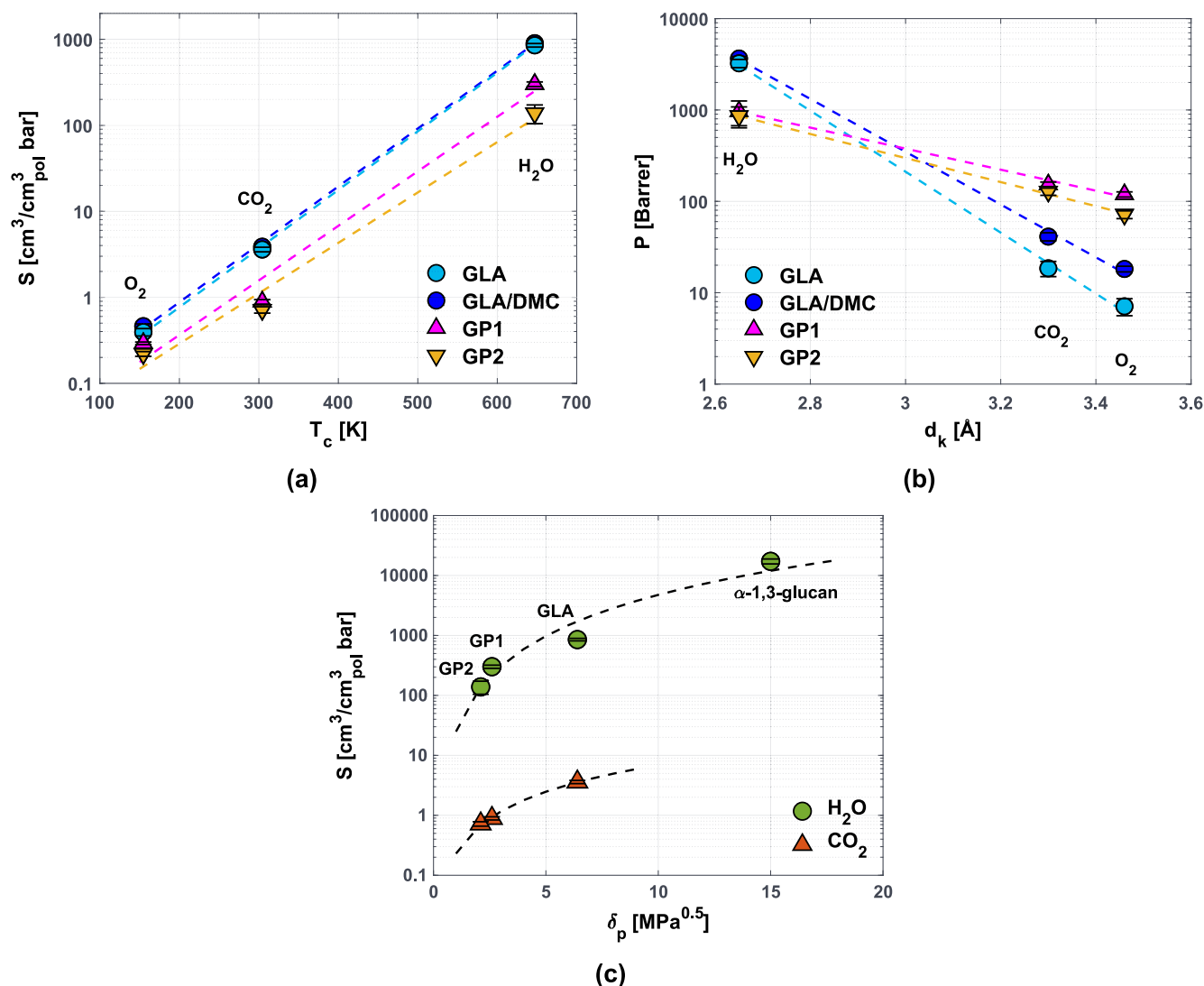


Fig. 5. Solubility and permeability of O_2 , CO_2 , and liquid water in GLA/ CHCl_3 , GLA/DMC, GP1/ CHCl_3 , and GP2/ CHCl_3 at 30 °C as function of penetrant properties: (a) Penetrant solubility as function of critical temperature, T_c ; (b) Permeability as function of kinetic diameter, d_k ; (c) Solubility of H_2O and CO_2 as function of the polar component of solubility parameter, δ_p , of α -1,3-glucan and its derivatives.

well with their molecular length-scale expressed as d_k , in the three materials investigated, as shown in Fig. 5b, with $P_{\text{H}_2\text{O}} > P_{\text{CO}_2} > P_{\text{O}_2}$. The permeability follows a decreasing trend with increasing size of the penetrant, suggesting that the kinetic diameter is the best parameter to describe transport properties of α -1,3-glucan esters. It is important to note, however, that permeability is not a function of kinetic diameter alone, with diffusivity and solubility having different relative contributions for different penetrants. It is possible to assess these contributions by comparing the relative ratios of solubility and permeability for $\text{H}_2\text{O}/\text{CO}_2$, $\text{H}_2\text{O}/\text{O}_2$ and CO_2/O_2 . Taking GLA cast from CHCl_3 as an example, water permeability is ~ 200 times greater than that of CO_2 and ~ 450 times greater than that of O_2 . Water solubility, on the other hand, is ~ 200 and ~ 2000 times as high, hence diffusivity contribution is close to neutral (~ 1) for $\text{H}_2\text{O}/\text{CO}_2$ performance or hindering (~ 0.2) for $\text{H}_2\text{O}/\text{O}_2$ performance. Similarly, CO_2 permeability is ~ 3 times higher than O_2 permeability, whereas CO_2 solubility is ~ 10 times higher and diffusivity ~ 4 times lower. Thus, the relative contributions of thermodynamic and kinetic parameters are largely dependent on the penetrant, with solubility driving the transport of water and CO_2 when this is compared to O_2 . The molecular size, expressed as kinetic diameter, simply emerges as a better descriptor of penetrant behaviour in this case, and evaluation of additional penetrants would be necessary for a more detailed

description of permeability dependence on molecular dimension and condensability.

The solubility of a gaseous penetrant can be attributed to the energetic interaction between the polymer and the penetrant (Matteucci et al., 2006). While $R_{C/O}$ can serve as a structural parameter to correlate a penetrant's solubility values, as shown later in the text (particularly in Section 3.6), a thermodynamic parameter like the polymer Hildebrand solubility parameter, δ , is typically used for this purpose. By definition, δ is the square root of the cohesive energy density, i.e., the cohesive energy per unit of molar volume of the polymer. For low molecular weight liquids, the cohesive energy density can be estimated from the vapourisation energy, while for polymers it is generally determined with group contribution approach. The cohesive energy can be divided into three parts to account for contribution of dispersion forces, polar forces, and hydrogen bonding. Thus, the solubility parameter can also be split in three components, δ_d , δ_p , and δ_h (Krevelen & Nijenhuis, 2009). Here, the three components of the solubility parameter were calculated for α -1,3-glucan and its derivatives according to Hoftyzer – Van Krevelen group contribution method (1976), with molar volume, V_m , estimated using Hoy's group contribution method (1985) (Krevelen & Nijenhuis, 2009). The detailed derivation is reported in Section S2 of the Supporting Information, while the dispersion, polar, and hydrogen bond energy

components, together with molar volumes of each functional group are reported in Table S2, with calculated values of the solubility parameter and its components included. The solubility of H₂O and CO₂ was found to follow an increasing trend with the polar component of the solubility parameter, δ_p , described through a power-law correlation, as shown in Fig. 5c:

$$S = S_0 \delta_p^n \quad (7)$$

The values of S_0 and n are reported in Table 4, together with the coefficient of determination, R^2 , for the two penetrants. It is noteworthy that the correlation identified for the liquid water solubility in esters of α -1,3-glucan can be easily extended to the unmodified polymer as well. This is not surprising, given that higher δ_p corresponds to higher hydrophilicity of the polymer and can thus be directly related to the structural parameters such as DoS or $R_{C/O}$. Indeed, δ_p was found to be inversely proportional to $R_{C/O}$, as shown in Fig. S2b, suggesting that the choice of either parameter is justified to correlate solubility properties of glucan-based materials. It is notable that, while S_0 and n depend on the specific method to calculate the cohesive energy and molar volume contributions, the general form of the solubility correlation with δ_p remains consistent if a different method is chosen.

3.5. Solvent influence on transport properties: chloroform vs dimethyl carbonate

The necessity to find sustainable alternatives in the field of membrane-based applications is not limited to the choice of polymeric materials, but it extends to the choice of the solvent used for thin film fabrication. The shift towards solvents characterised by a more environmentally friendly production and lower final toxicity is needed to improve the overall sustainability of membrane processes (Dong et al., 2021; Figoli et al., 2014). However, the use of different solvents for membrane production could affect the resulting material properties, including mechanical, thermal, and transport ones (Li et al., 2013; Papchenko et al., 2022).

Here, a brief discussion is provided on transport properties in membranes of GLA cast from Chloroform, a typical petroleum-based solvent, and Dimethyl Carbonate (DMC), a greener alternative (Jessop, 2011; Pyo et al., 2017). The two membrane samples, GLA/CHCl₃ and GLA/DMC, shown in Fig. 1b and c (Section 3.1), present no observable differences in film flexibility or transparency by the naked eye.

When transport properties are investigated, water wettability, as well as water solubility, diffusivity, and permeability in GLA/CHCl₃ and GLA/DMC are found to be equal within the experimental error, as shown in Fig. 5 and reported in Table 5 (Section 3.6). However, when CO₂ and O₂ transport is investigated, the solubility of the two gases is not affected by the solvent, while the diffusion coefficient (Fig. 5b) increases by a factor of 2 in the GLA/DMC sample for both CO₂ and O₂. The observed effect could be attributed to the differences in membrane preparation conditions. A higher evaporation temperature is required for membrane formation when DMC is used as a solvent (30 °C), compared to chloroform (room temperature, ~20 °C), to compensate for a higher boiling temperature of DMC (90 °C and 61 °C, respectively). Therefore, the evaporation rate of the two solvents might be different at their respective casting temperatures, influencing film formation kinetics and final morphology. The higher processing temperature used for DMC might

reduce the polymer chain relaxation time during casting, leading to a higher free volume in the final DMC-based samples, a phenomenon that is observed in glassy amorphous films like GLA (Figoli et al., 2014; Li et al., 2013). Free volume variations can have a dramatic effect on gas molecules diffusion, which here translates into diffusion coefficients of CO₂ and O₂ molecules twice as high in the sample cast from DMC with respect to chloroform. The water diffusivity on the other hand, due to its small molecular size, is not highly reliant on the free volume increase induced by the solvent. The solubility as a property, regardless of the molecule size, is not greatly affected by the free volume, as it is mostly dominated by penetrant-polymer interactions which change only with chemical structure.

The higher diffusivity coefficients of CO₂ and O₂ in the GLA/DMC sample lead to permeability values that are more than twice those in the GLA/CHCl₃ sample. The ideal permselectivity, on the other hand, is ultimately not affected by the solvent choice, being equal to 2.6 and 2.3 when Chloroform or DMC is used respectively. This is mainly due to the fact that the diffusion of both gases is increased by the same factor when DMC is used for casting.

3.6. Transport properties comparison with other materials

Transport of liquid water in polysaccharides represents an important aspect of their applicability to different sectors, with membrane-based separations and food packaging being some of them. Thus, the ability to predict a property based on a structural parameter becomes essential in order to inform future developments of polysaccharide-based materials. Here, we want to understand if a single structural parameter can offer a simplified but useful tool to describe the equilibrium water sorption in different classes of polysaccharides. For this purpose, we introduced a relevant structural parameter, $R_{C/O}$, the C/O functional group ratio, that can be used to describe main properties of glucan-based materials, including mixed esters. We found that the equilibrium water uptake c_W in [g/g_{pol} %] at 100% RH can be described with good accuracy through a power-law correlation ($R^2 = 0.913$) in glucan-based materials investigated here, as shown in Fig. 6:

$$c_W = 59.9 R_{C/O}^{-2.2} \quad (8)$$

Given the structural similarity between α -1,3-glucan and cellulose, a hypothesis has been made where a similar correlation could describe water uptake in cellulose-based materials with aliphatic substituents, using $R_{C/O}$ as parameter to include mixed esters in the present investigation. Using values taken from literature (Aulin et al., 2010; Chalykh et al., 2021; Nilsson et al., 2022; Ong et al., 2013), a following correlation was found for cellulose-based materials: $c_W = 72.6 R_{C/O}^{-2.6}$ ($R^2 = 0.826$), valid for values of $R_{C/O}$ up to the highest value reported here of 3.3. Comparison between the two correlations in the range of C/O functional group ratios of 1.2 to 3.3 allows to quantify the effect of the backbone linkage difference in the two polysaccharides. The deviation between the two predictions is between 10% and 30%, with the highest difference present at the highest $R_{C/O}$ equal to 3.3. This deviation, however, is much lower than the water uptake decrease predicted by both correlations in the same interval of C/O functional group ratios and equal to 89% and 93% for glucan-based and cellulose-based materials respectively.

Given that Eq. 8 can describe glucan esters in the range of $R_{C/O}$ up to 8.6, its applicability to cellulose esters was tested as well, returning a similar accuracy seen for glucan-based materials ($R^2 = 0.919$). Hence, the power-law correlation introduced for glucan-based materials can accurately represent water sorption variation with degree of esterification in glucan-based and cellulose-based materials up to relatively high values of $R_{C/O}$.

The quantitative structure-property correlation presented here allows to quantify and predict the extent of water uptake variation at 100% RH upon structural modification of hypothetical polysaccharide

Table 4

Parameters of Eq. 7 for H₂O and CO₂ solubility in α -1,3-glucan and its derivatives as function of the polar component of the solubility parameter of the investigated polymers.

Penetrant	S_0 [cm ³ /cm ³ _{pol} bar]	n [–]	R^2
H ₂ O	24.9	2.28	0.866
CO ₂	0.23	1.48	0.999

Table 5

Transport properties of different penetrants in α -1,3-glucan and its esters at 30 °C. Water properties are from gravimetric sorption at 100% RH. *Transport properties of CO₂ and O₂ in GLA/CHCl₃ and GLA/DMC are estimated at equilibrium pressure of 1 bar through interpolation of sorption data. Data for PLA (L:D 100:0, 20 °C for water; L:D 98.7:1.3, 30 °C for gases) and for PET (25 °C) are taken from literature (Bao et al., 2006; Gouanvé et al., 2007; Liu et al., 2004; McGonigle et al., 2001; Siparsky et al., 1997).

		H ₂ O	CO ₂	O ₂
α -1,3-glucan	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	$(1.70 \pm 0.16) \times 10^4$ ($(5.3 \pm 0.5) \times 10^{-1}$)	—	—
	D [cm ² /s]	$(1.5 \pm 0.3) \times 10^{-7}$	—	—
	P [Barrer] (WP [g mm/m ² day])	$(3.3 \pm 0.7) \times 10^5$ ($(7.4 \pm 1.8) \times 10^2$)	—	—
GLA/CHCl ₃ *	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	$(8.5 \pm 0.4) \times 10^2$ ($(2.8 \pm 0.1) \times 10^{-2}$)	$(3.6 \pm 0.2) \times 10^0$	$(3.9 \pm 0.4) \times 10^{-1}$
	D [cm ² /s]	$(2.9 \pm 0.3) \times 10^{-8}$	$(3.84 \pm 0.69) \times 10^{-8}$	$(1.36 \pm 0.26) \times 10^{-7}$
	P [Barrer] (WP [g mm/m ² day])	$(3.2 \pm 0.3) \times 10^3$ ($(7.2 \pm 1.0) \times 10^0$)	$(1.85 \pm 0.35) \times 10^1$	$(7.1 \pm 1.5) \times 10^0$
GLA/DMC*	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	$(9.0 \pm 0.4) \times 10^2$ ($(3.0 \pm 0.1) \times 10^{-2}$)	$(3.97 \pm 0.17) \times 10^0$	$(4.6 \pm 0.3) \times 10^{-1}$
	D [cm ² /s]	$(3.1 \pm 0.1) \times 10^{-8}$	$(7.8 \pm 0.7) \times 10^{-8}$	$(2.96 \pm 0.09) \times 10^{-7}$
	P [Barrer] (WP [g mm/m ² day])	$(3.7 \pm 0.2) \times 10^3$ ($(8.1 \pm 0.5) \times 10^0$)	$(4.1 \pm 0.4) \times 10^1$	$(1.8 \pm 0.1) \times 10^1$
GP1/CHCl ₃	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	$(3.0 \pm 0.2) \times 10^2$ ($(1.31 \pm 0.08) \times 10^{-2}$)	$(8.9 \pm 0.5) \times 10^{-1}$	$(2.9 \pm 0.1) \times 10^{-1}$
	D [cm ² /s]	$(2.4 \pm 0.7) \times 10^{-8}$	$(1.29 \pm 0.03) \times 10^{-6}$	$(3.1 \pm 0.2) \times 10^{-6}$
	P [Barrer] (WP [g mm/m ² day])	$(9.6 \pm 2.9) \times 10^2$ ($(2.1 \pm 0.6) \times 10^0$)	$(1.5 \pm 0.1) \times 10^2$	$(1.19 \pm 0.08) \times 10^2$
GP2/CHCl ₃	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	$(1.4 \pm 0.3) \times 10^2$ ($(5.45 \pm 1.34) \times 10^{-3}$)	$(7.2 \pm 0.6) \times 10^{-1}$	$(2.2 \pm 0.1) \times 10^{-1}$
	D [cm ² /s]	$(4.7 \pm 0.4) \times 10^{-8}$	$(1.34 \pm 0.04) \times 10^{-6}$	$(2.4 \pm 0.2) \times 10^{-6}$
	P [Barrer] (WP [g mm/m ² day])	$(8.6 \pm 2.2) \times 10^2$ ($(1.9 \pm 0.5) \times 10^0$)	$(1.3 \pm 0.1) \times 10^2$	$(7.2 \pm 0.7) \times 10^1$
PLA	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	4.00×10^2 (1.4×10^{-2})	1.86×10^0	3.68×10^{-2}
	D [cm ² /s]	4.00×10^{-8}	4.40×10^{-9}	5.70×10^{-8}
	P [Barrer] (WP [g mm/m ² day])	2.1×10^3 (4.7×10^0)	1.10×10^0	2.60×10^{-1}
PET	S [cm ³ (STP)/cm ³ pol bar] (c_w [g/g _{pol}])	7.50×10^2 (5.43×10^{-3})	1.02×10^0	9.67×10^{-2}
	D [cm ² /s]	1.00×10^{-9}	1.07×10^{-9}	5.60×10^{-9}
	P [Barrer] (WP [g mm/m ² day])	1.00×10^2 (2.20×10^{-1})	1.46×10^{-1}	7.22×10^{-2}

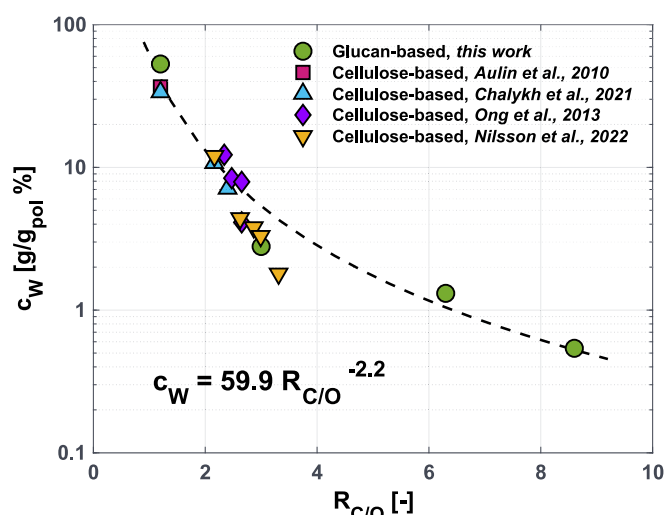


Fig. 6. Equilibrium water uptake, c_w , at 100% RH, as function of functional group ratio $R_{C/O}$ in glucan-based polysaccharides investigated in this work and cellulose-based polysaccharides from literature (Aulin et al., 2010; Chalykh et al., 2021; Nilsson et al., 2022; Ong et al., 2013), described by the correlation defined in Eq. 8. Error bars are not shown for the sake of clarity.

aliphatic esters. As discussed in Section 3.2, the increase in DoS of the long-chain substituent, as well as in the side-chain length, plays a major role in the equilibrium water uptake, as it ultimately reduces the number and accessibility of functional groups able to interact with water. Given the overall structural similarity of different polysaccharides, the total distribution of functional groups in their ester dictates the availability of interaction sites, side-chain steric hindrance, and potential presence of side-chain crystalline domains. It can be unambiguously represented by $R_{C/O}$, in particular when a mixture of substituents is present and the correlation with other structural parameters fails to capture the general trend, like in the case DoS of the hydroxyl group.

The provided water sorption model based on a single structural descriptor is not intended to accurately describe water interaction with the polysaccharide, but rather to offer a simple tool to estimate equilibrium water uptake at 100% RH in its aliphatic derivatives. This model

also shows that it is possible to use a single structural parameter to describe the behaviour of mixed esters in two different classes in polysaccharides. The correlation proposed here represents the much-needed preliminary step for predicting water transport in polysaccharides and towards the development of a method for tailoring the desired structural properties. The use of this tool and the development of additional correlations accounting for water kinetics, performance at varying levels of humidity as well as in mixed-gas conditions, anticipates accelerating substantial development of glucan- and cellulose-based materials for applications where water transport represents a relevant criterion for material choice.

When CO₂ and O₂ properties are considered, a Robeson plot can be a useful tool for the comparison of different materials separation properties, where the permselectivity between two gases is reported against the

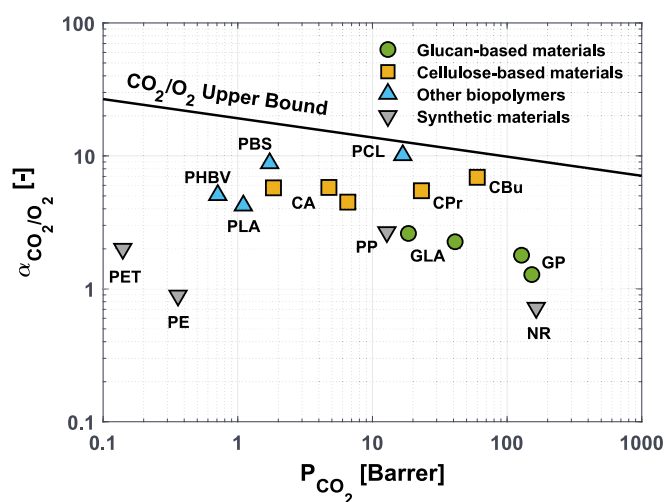


Fig. 7. Robeson plot for CO₂/O₂ separation with glucan-based materials investigated in this work reported together with literature data for cellulose-based materials (Chen et al., 2014; Puleo et al., 1989), other biopolymers (Bao et al., 2006; Ferri et al., 2023; Messin et al., 2020; Mogri & Paul, 2001), and non-bio polymers (Goodarzi et al., 2013; McGonigle et al., 2001; Michaels & Bixler, 1961). The derived Upper Bound for CO₂/O₂ separation (Eq. 9) is reported for comparison. Error bars are not shown for the sake of clarity.

permeability of the most permeable one. Fig. 7 shows the Robeson plot for CO₂/O₂ separation, with glucan esters investigated in this work compared to other relevant polymers, such as cellulose-based materials (Chen et al., 2014; Puleo et al., 1989), other biopolymers (Bao et al., 2006; Ferri et al., 2023; Messin et al., 2020; Mogri & Paul, 2001), in particular PHBV, PLA, PBS, and PCL, and synthetic polymers (Goodarzi et al., 2013; McGonigle et al., 2001; Michaels & Bixler, 1961), such as PE, and its amorphous analogue, natural rubber (NP). The Upper Bound represents the intrinsic limitation of polymeric membranes to achieve high permeability and permselectivity simultaneously, and the CO₂/O₂ upper bound is here derived based on CO₂/N₂ and O₂/N₂ upper bounds from 2008 (Robeson, 2008) and shown in Fig. 7 for comparison purposes. The detailed derivation of the CO₂/O₂ upper bound is described in Section S5 of the Supporting Information, while it can be expressed as:

$$P_{\text{CO}_2} = k_{\text{CO}_2/\text{O}_2} \alpha_{\text{CO}_2/\text{O}_2}^{n_{\text{CO}_2/\text{O}_2}} = 776623860 \alpha_{\text{CO}_2/\text{O}_2}^{-6.93} \quad (9)$$

Such upper bound was not presented in the works of Robeson (Robeson, 2008; Robeson et al., 2009, 2014). To the best of our knowledge, while it has been graphically reported as a comparison tool (Basdogan et al., 2024; Kanehashi et al., 2013), its exact expression is published in this work for the first time.

Glucan esters show high CO₂ permeabilities, comparable with those in cellulose propionate (CPr) and cellulose butyrate (CBu), and Natural Rubber (NR). As discussed in Section 3.3, this is due mostly to the effect of long-chain substituents on CO₂ solubility and diffusivity. Indeed, GP1 and GP2, which differ only on their DoS, are characterised by very similar CO₂ solubilities with CO₂ diffusivity values similar to those observed in NR. The permselectivity of glucan esters, however, is on average higher or comparable to those found in non-bio polymers, but lower than in cellulose-based polymers and other biopolymers of relevance. Analysis of CO₂/O₂ behaviour in short-chain glucan esters would allow for a more direct comparison with cellulose acetates (CA), CPr, and CBu. It could also help identify the side-chain length at which CO₂ permeability shifts from being mostly influenced by the backbone properties to being mainly affected by the presence of the aliphatic side chain. Based on the observations presented in this work for long-chain glucan esters, short-chain glucan esters are expected to exhibit a lower CO₂ permeability when compared to long-chain ones, as they would present increased availability of sorption sites but decreased diffusivity. The CO₂/O₂ selectivity on the other hand, should remain fairly constant across compositions, if the same trend of cellulose esters is followed. Such assumption is reasonable given the similarity in water and CO₂ behaviour in the two classes of polysaccharides. The data for short-chain glucan esters, however, are currently unavailable and should be object of future work in order to verify this behaviour. Same is true for long-chain cellulose esters, where performance comparison against the materials explored here can suggest future application directions.

Last, Table 5 summarises and allows to compare the permeability values of H₂O, CO₂, and O₂ in esters of α-1,3-glucan to PLA, a biopolymer currently used in various applications at the commercial level, and with those of PET, a widely used polymer in textile, injection moulding and rigid and flexible packaging (Bao et al., 2006; Gouanvé et al., 2007; Liu et al., 2004; McGonigle et al., 2001; Siparsky et al., 1997). Overall, permeability values for all penetrants are up to several orders of magnitude higher in glucan esters compared to commercial polymers, with water permeability values of GP1 and GP2 approaching those of PLA but being an order of magnitude higher than those of PET. This is due to diffusivity values being substantially higher in glucan esters with respect to both PLA and PET. The same applies for CO₂ and O₂ transport: while GP1 and GP2 offer comparable gas solubilities, their diffusion coefficients are much higher than those of reference polymers, probably because they are amorphous and apolar while both PLA and PET are both semicrystalline and offer favourable interaction sites to CO₂ molecules, which are known to reduce the diffusivity of such gas.

Overall, glucan-based materials have shown promising tuneable

transport properties widening the range of potential applications. The water uptake suppression in long-chain glucan esters paves the way to their application as food packaging films. Meanwhile, the ability to control CO₂/O₂ permselectivity by adjusting the structure of glucan esters becomes beneficial for the same application, in particular for modified atmosphere packaging. Here, it is important to match the film's gas separation behaviour to the products' respiration rate. For example, CO₂/O₂ permselectivity close to unity can prevent anaerobic fermentation, while higher values would prevent oxidation in addition to the further CO₂ excess removal (Al-Ati & Hotchkiss, 2003). High CO₂ permeability in glucan palmitates suggests gas membrane separation as another suitable application, where they could be used to treat CO₂ mixtures with other gases. For example, the membranes currently used in most CO₂ separation plants are based on cellulose acetate and present pure-gas CO₂ permeability lower than 10 Barrer, while their CO₂/CH₄ selectivity ranges between 30 and 10 (Baker & Low, 2014). Increasing permeability without lowering selectivity would allow for a much more efficient separation. In addition, commercial gas membranes used for CO₂/N₂ separation present CO₂ permeabilities of ~100 Barrer (assuming membrane thickness of 1 μm) and selectivities of ~20 (Merkel et al., 2010), although permeabilities of ~1000 Barrer are currently explored for the application.

4. Conclusions

The present work provides the first quantification of liquid water sorption and transport properties in unmodified α-1,3-glucan and its three esters, glucan laurate acetate (GLA) and glucan palmitates (GP1, GP2), and their relation with the different degree of substitution (DoS). In addition, CO₂, and O₂ sorption and transport are investigated in GLA, GP1, and GP2. Glucan-based materials offer the unique advantage of being produced via enzymatic polymerisation from sucrose, offering an easily scalable solution for biodegradable replacement in several applications.

Here, we introduce a new structural parameter, the C/O functional group ratio, $R_{\text{C/O}}$, which is inversely proportional to the polar solubility parameter, δ_p . We use $R_{\text{C/O}}$ to correlate transport properties in glucan-based materials, as it allows to easily include mixed esters in the analysis. The tests revealed that the liquid water uptake decreases markedly with increasing DoS of the long-chain substituent and $R_{\text{C/O}}$, varying from 53% in weight in the unmodified polymer to 0.5% in GP2. Similarly, the contact angle increases with $R_{\text{C/O}}$, with θ_0 reaching 87° in GP2 with respect to 39° for α-1,3-glucan, as expected due to the lower hydrophilicity of the more substituted polymers. Water vapour tests, carried out at increasing values of relative humidity for glucan esters, confirm the behaviour observed during liquid water sorption tests and allow to determine the shape of solubility isotherms in the whole humidity range. The liquid water diffusion coefficient is found to be less sensitive to the type and extent of substitution. The liquid water permeability was estimated as the product of solubility and diffusivity and showed a significant decrease due to esterification of α-1,3-glucan, with GP2 reaching a value of ~2 g mm/m² day at 100% RH, a value 400 times lower compared to the unmodified glucan. Such outcome indicates that the water permeability is mostly driven by solubility effects, but it also represents the first qualitative correlation between water barrier effect and chemical structure in glucan materials.

CO₂ and O₂ gas solubilities and diffusivities were measured for the three glucan esters in a pressure decay manometric apparatus. Both solubility and diffusivity were found to be mostly affected by the chain length of the substituent rather than by the properties of the backbone. CO₂ and O₂ permeabilities, estimated as product of gas solubility and diffusivity, seem to increase with the side-chain length, but not as regularly as observed in cellulose esters. CO₂/O₂ permselectivity was found to be in the range between 3 and 1 for the three esters, with CO₂/O₂ solubility-selectivity reaching a value of ~10 in GLA at low pressures.

Glucan esters investigated here were found to be CO₂-selective, with values of CO₂ permeability ranging over an order of magnitude. In particular, CO₂ permeability in glucan palmitates was found to be higher than 100 Barrer (3.34×10^{-14} mol m/(m² s Pa)), which suggests a need for future assessment of their suitability for gas membrane separations of industrial relevance, such as natural gas sweetening and post-combustion carbon capture.

We were able to replace the solvent used for GLA-based films cast, substituting chloroform with the greener DMC. Not only this solvent allows to obtain films that are undistinguishable from the ones made from chloroform, but such samples also exhibit similar water transport. The only difference was found in the CO₂ and O₂ diffusivity and permeability, which increased by a factor of 2 in the membrane cast from DMC, due a similar increase in gas diffusivities, with no repercussion on the ideal CO₂/O₂ permselectivity. This was attributed to the higher evaporation temperature used for DMC, which induces a higher free volume in the final amorphous glassy film, which affects most significantly the diffusion.

Given the structural similarity between α -1,3-glucan and cellulose, we were able to derive the inverse power-law correlation between the liquid water uptake and $R_{C/O}$, valid for both families of polysaccharides. This simple quantitative structure-property relationship can be leveraged to estimate liquid water uptake in hypothetical cellulose-based and glucan-based materials based only on their structure, leading to an accelerated development trajectory for applications where water transport is a key factor in material selection.

Finally, we used the CO₂/O₂ Robeson plot with explicitly derived upper bound to compare the performance of glucan-based materials with cellulose-based materials, common bio-polymers, and commercial materials currently used for food packaging. Environmentally friendly glucan-based materials inspected here showed higher CO₂ permeabilities with respect to other materials, with CO₂/O₂ selectivities comparable to those of petroleum-based polymers such as PP and PET. Similarly, water permeability was found to be comparable in GPs and PLA, although higher than in PET. As opposed to conventional materials with generally fixed properties, glucan-based polymers combine intrinsic sustainability and scalability with tunability through a single structural variable over an exceptionally wide range of performances for H₂O, CO₂, and O₂. Hence, this bio-based tunability represents a novel potential platform for a sustainable membrane design.

The present study sets the ground for future investigations of glucan-based sustainable materials with lower environmental footprint and with focus on applications where the material shows promising strength such as membrane-based separations.

CRediT authorship contribution statement

Kseniya Papchenko: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Investigation, Formal analysis, Data curation. **Kyriaki Lampri:** Investigation, Data curation. **Giulio Santori:** Writing – review & editing, Validation, Resources, Methodology, Formal analysis. **Janice To:** Investigation, Data curation. **Daniel Orejon:** Writing – review & editing, Validation, Resources, Methodology, Formal analysis. **Natnael Behabtu:** Writing – review & editing, Validation, Resources, Project administration, Funding acquisition, Conceptualization. **Jure Zlopasa:** Writing – review & editing, Validation, Resources, Methodology. **Maria Grazia De Angelis:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbpol.2026.125296>.

Data availability

Data will be made available on request.

References

- Aadibi, A., Valdesueiro, D., Mok, J., Behabtu, N., Lenges, C., Simon, L., & Mekonnen, T. H. (2022). Sustainable barrier paper coating based on alpha-1,3 glucan and natural rubber latex. *Carbohydrate Polymers*, 282, Article 119121. <https://doi.org/10.1016/j.carbpol.2022.119121>
- Al Balushi, K. M., Sefiane, K., & Orejon, D. (2022). Binary mixture droplet wetting on micro-structure decorated surfaces. *Journal of Colloid and Interface Science*, 612, 792–805. <https://doi.org/10.1016/j.jcis.2021.12.171>
- Al-Ati, T., & Hotchkiss, J. H. (2003). The role of packaging film permselectivity in modified atmosphere packaging. *Journal of Agricultural and Food Chemistry*, 51(14), 4133–4138. <https://doi.org/10.1021/jf034191b>
- ASTM D1434-82(2015)e1. (2015). *Test method for determining gas permeability characteristics of plastic film and sheeting* (ICS Code 83.140.10). ASTM International. <https://doi.org/10.1520/D1434-82R15E01>
- ASTM D570-22. (2022). *Standard test method for water absorption of plastics* (ICS Code 83.120). ASTM International. <https://doi.org/10.1520/D0570-22>
- Aulin, C., Gällstedt, M., & Lindström, T. (2010). Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. *Cellulose*, 17(3), 559–574. <https://doi.org/10.1007/s10570-009-9393-y>
- Baker, R. W., & Low, B. T. (2014). Gas separation membrane materials: A perspective. *Macromolecules*, 47(20), 6999–7013. <https://doi.org/10.1021/ma501488s>
- Bao, L., Dorgan, J. R., Knauss, D., Hait, S., Oliveira, N. S., & Maruccio, I. M. (2006). Gas permeation properties of poly(lactic acid) revisited. *Journal of Membrane Science*, 285 (1–2), 166–172. <https://doi.org/10.1016/j.memsci.2006.08.021>
- Basdogan, Y., Pollard, D. R., Shastry, T., Carbone, M. R., Kumar, S. K., & Wang, Z.-G. (2024). Machine learning-guided discovery of polymer membranes for CO₂ separation with genetic algorithm. *Journal of Membrane Science*, 712, Article 123169. <https://doi.org/10.1016/j.memsci.2024.123169>
- Behabtu, N., & Kralj, S. (2020). Enzymatic polymerization routes to synthetic–natural materials: A review. *ACS Sustainable Chemistry & Engineering*, 8(27), 9947–9954. <https://doi.org/10.1021/acssuschemeng.0c01664>
- Bernardo, P., Drioli, E., & Golemme, G. (2009). Membrane gas separation: A review/state of the art. *Industrial & Engineering Chemistry Research*, 48(10), 4638–4663. <https://doi.org/10.1021/ie8019032>
- Caimi, P. G., Hennessey, S. M., Nagy, K. D., & Payne, M. S. (2015). *Process for producing alpha-1,3-glucan polymer with reduced molecular weight* (patent no. US9169506B2).
- Chalykh, A. E., Bardyshev, I. I., & Petrova, T. F. (2021). Free volume and water sorption by cellulose esters. *Polymers*, 13(16), 2644. <https://doi.org/10.3390/polym13162644>
- Chen, J., Zhang, J., Feng, Y., He, J., & Zhang, J. (2014). Effect of molecular structure on the gas permeability of cellulose aliphatic esters. *Chinese Journal of Polymer Science*, 32(1), 1–8. <https://doi.org/10.1007/s10118-014-1384-2>
- Crank, J. (1979). *The mathematics of diffusion*. Oxford University Press.
- Crépy, L., Miri, V., Joly, N., Martin, P., & Lefebvre, J.-M. (2011). Effect of side chain length on structure and thermomechanical properties of fully substituted cellulose fatty esters. *Carbohydrate Polymers*, 83(4), 1812–1820. <https://doi.org/10.1016/j.carbpol.2010.10.045>
- Dong, X., Lu, D., Harris, T. A. L., & Escobar, I. C. (2021). Polymers and solvents used in membrane fabrication: A review focusing on sustainable membrane development. *Membranes*, 11(5), 309. <https://doi.org/10.3390/membranes11050309>

- Drioli, E., Macedonio, F., & Tocci, E. (2021). Membrane science and membrane engineering for a sustainable industrial development. *Separation and Purification Technology*, 275, Article 119196. <https://doi.org/10.1016/j.seppur.2021.119196>
- Ferrari, M. C., Galizia, M., De Angelis, M. G., & Sarti, G. C. (2010). Gas and vapor transport in mixed matrix membranes based on amorphous Teflon AF1600 and AF2400 and fumed silica. *Industrial & Engineering Chemistry Research*, 49(23), 11920–11935. <https://doi.org/10.1021/ie100242q>
- Ferri, M., Papchenko, K., Degli Esposti, M., Tondi, G., De Angelis, M. G., Morselli, D., & Fabbri, P. (2023). Fully biobased polyhydroxyalkanoate/tannin films as multifunctional materials for smart food packaging applications. *ACS Applied Materials & Interfaces*, 15(23), 28594–28605. <https://doi.org/10.1021/acsami.3c04611>
- Figoli, A., Marino, T., Simone, S., Di Nicolò, E., Li, X.-M., He, T., & Drioli, E. (2014). Towards non-toxic solvents for membrane preparation: A review. *Green Chemistry*, 16(9), 4034–4059. <https://doi.org/10.1039/C4GC00613E>
- Geitel, K., Koschella, A., Lenges, C., & Heinze, T. (2020). Melttable fatty acid esters of α -1,3-glucan as potential thermoplastics. *Advanced Industrial and Engineering Polymer Research*, 3(3), 111–119. <https://doi.org/10.1016/j.aiepr.2020.07.004>
- Geyer, R. (2020). Production, use, and fate of synthetic polymers. In *Plastic waste and recycling* (pp. 13–32). Elsevier. <https://doi.org/10.1016/B978-0-12-817880-5.00002-5>
- Ghosal, K., Chern, R. T., Freeman, B. D., Daly, W. H., & Negulescu, I. I. (1996). Effect of basic substituents on gas sorption and permeation in polysulfone. *Macromolecules*, 29(12), 4360–4369. <https://doi.org/10.1021/ma951310i>
- Goodarzi, V., Hassan Jafari, S., Ali Khonakdar, H., Ghalei, B., & Mortazavi, M. (2013). Assessment of role of morphology in gas permselectivity of membranes based on polypropylene/ethylene vinyl acetate/clay nanocomposite. *Journal of Membrane Science*, 445, 76–87. <https://doi.org/10.1016/j.memsci.2013.04.073>
- Gouanvé, F., Marais, S., Bessadok, A., Langevin, D., & Métayer, M. (2007). Kinetics of water sorption in flax and PET fibers. *European Polymer Journal*, 43(2), 586–598. <https://doi.org/10.1016/j.eurpolymj.2006.10.023>
- Grzybek, P., Dudek, G., & Van Der Bruggen, B. (2024). Cellulose-based films and membranes: A comprehensive review on preparation and applications. *Chemical Engineering Journal*, 495, Article 153500. <https://doi.org/10.1016/j.cej.2024.153500>
- Heinze, T. (2015). Cellulose: Structure and properties. In O. J. Rojas (Ed.), 271. *Cellulose chemistry and properties: Fibers, nanocelluloses and advanced materials* (pp. 1–52). Springer International Publishing. https://doi.org/10.1007/12_2015_319
- Heinze, T., El Seoud, O. A., & Koschella, A. (2018). Cellulose esters. In T. Heinze, O. A. El Seoud, & A. Koschella (Eds.), *Cellulose derivatives* (pp. 293–427). Springer International Publishing. https://doi.org/10.1007/978-3-319-73168-1_5
- Heinze, T., Pfeifer, A., Koschella, A., Adelman, D., Howe, L., Behabtu, N., & Lenges, C. (2019). Engineered polysaccharides: α -1,3-glucan acetates showing upper critical solution temperature in organic solvents. *Macromolecular Chemistry and Physics*, 220(16), Article 1900112. <https://doi.org/10.1002/macp.201900112>
- Jessop, P. G. (2011). Searching for green solvents. *Green Chemistry*, 13(6), 1391. <https://doi.org/10.1039/c0gc00797h>
- Kanehashi, S., Kishida, M., Kidesaki, T., Shindo, R., Sato, S., Miyakoshi, T., & Nagai, K. (2013). CO₂ separation properties of a glassy aromatic polyimide composite membranes containing high-content 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonfyl)imide ionic liquid. *Journal of Membrane Science*, 430, 211–222. <https://doi.org/10.1016/j.memsci.2012.12.003>
- Kasat, R. B., & Paullin, J. L. (2016). Preparation of poly α -1,3-glucan esters and films made therefrom (patent no. U.S. patent US9278988B2).
- Kim, J., Qudsi, Y. H., Mok, J., Lenges, C., & Simon, L. (2023). Engineered polysaccharide α -1,3-glucan in highly filled thermoplastic polyurethane systems. *Journal of Applied Polymer Science*, 140(43), Article e54051. <https://doi.org/10.1002/app.54051>
- Krevelen, D. W. v., & Nijenhuis, K. t. (2009). *Properties of polymers: Their correlation with chemical structure: Their numerical estimation and prediction from additive group contributions* (4th, completely rev. ed.). Elsevier.
- Law, K.-Y. (2014). Definitions for hydrophilicity, hydrophobicity, and superhydrophobicity: Getting the basics right. *The Journal of Physical Chemistry Letters*, 5(4), 686–688. <https://doi.org/10.1021/jz402762h>
- Li, P., Chung, T. S., & Paul, D. R. (2013). Gas sorption and permeation in PIM-1. *Journal of Membrane Science*, 432, 50–57. <https://doi.org/10.1016/j.memsci.2013.01.009>
- Liu, R. Y. F., Hu, Y. S., Schiraldi, D. A., Hiltner, A., & Baer, E. (2004). Crystallinity and oxygen transport properties of PET bottle walls. *Journal of Applied Polymer Science*, 94(2), 671–677. <https://doi.org/10.1002/app.20905>
- Liu, T., Ren, Q., Wang, S., Gao, J., Shen, C., Zhang, S., ... Guan, F. (2023). Chemical modification of polysaccharides: A review of synthetic approaches, biological activity and the structure–activity relationship. *Molecules*, 28(16), Article 6073. <https://doi.org/10.3390/molecules28166073>
- Luberti, M., Olkis, C., Bensted, G., & Santori, G. (2020). Water sorption equilibrium on 2-hydroxyethyl-trimethylammonium acetate in the temperature range 298.25–349.55K. *Fluid Phase Equilibria*, 522, Article 112758. <https://doi.org/10.1016/j.fluid.2020.112758>
- Mangaraj, S., Yadav, A., Bal, L. M., Dash, S. K., & Mahanti, N. K. (2019). Application of biodegradable polymers in food packaging industry: A comprehensive review. *Journal of Packaging Technology and Research*, 3(1), 77–96. <https://doi.org/10.1007/s41783-018-0049-y>
- Matteucci, S., Yampolskii, Y., Freeman, B. D., & Pinnau, I. (2006). Transport of gases and vapors in glassy and rubbery polymers. In Y. Yampolskii, I. Pinnau, & B. Freeman (Eds.), *Materials science of membranes for gas and vapor separation* (1st ed., pp. 1–47). Wiley. <https://doi.org/10.1002/047002903X.ch1>
- McGonigle, E.-A., Liggit, J. J., Pethrick, R. A., Jenkins, S. D., Daly, J. H., & Hayward, D. (2001). Permeability of N₂, Ar, He, O₂ and CO₂ through biaxially oriented polyester films—Dependence on free volume. *Polymer*, 42(6), 2413–2426. [https://doi.org/10.1016/S0032-3861\(00\)00615-7](https://doi.org/10.1016/S0032-3861(00)00615-7)
- Meriçer, Ç., Minelli, M., Giacinti Baschetti, M., & Lindström, T. (2017). Water sorption in microfibrillated cellulose (MFC): The effect of temperature and pretreatment. *Carbohydrate Polymers*, 174, 1201–1212. <https://doi.org/10.1016/j.carbpol.2017.07.023>
- Merkel, T. C., Lin, H., Wei, X., & Baker, R. (2010). Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *Journal of Membrane Science*, 359(1–2), 126–139. <https://doi.org/10.1016/j.memsci.2009.10.041>
- Messin, T., Marais, S., Follain, N., Guinault, A., Gaucher, V., Delpouve, N., & Sollogoub, C. (2020). Biodegradable PLA/PBS multilayer membrane with enhanced barrier performances. *Journal of Membrane Science*, 598, Article 117777. <https://doi.org/10.1016/j.memsci.2019.117777>
- Michaels, A. S., & Bixler, H. J. (1961). Flow of gases through polyethylene. *Journal of Polymer Science*, 50(154), 413–439. <https://doi.org/10.1002/pol.1961.1205015412>
- Minelli, M., Cocchi, G., Ansaloni, L., Baschetti, M. G., De Angelis, M. G., & Doghieri, F. (2013). Vapor and liquid sorption in matrimid polyimide: Experimental characterization and modeling. *Industrial & Engineering Chemistry Research*, 52(26), 8936–8945. <https://doi.org/10.1021/ie3027873>
- Mishra, V., & Dennes, T. J. (2018). Production of poly α -1,3-glucan films (patent no. U. S. patent US10059778B2).
- Moffat, R. J. (1988). Describing the uncertainties in experimental results. *Experimental Thermal and Fluid Science*, 1(1), 3–17. [https://doi.org/10.1016/0894-1777\(88\)90043-X](https://doi.org/10.1016/0894-1777(88)90043-X)
- Mogri, Z., & Paul, D. R. (2001). Gas sorption and transport in poly(alkyl (meth)acrylate)s. I. Permeation properties. *Polymer*, 42(18), 7765–7780. [https://doi.org/10.1016/S0032-3861\(01\)00260-9](https://doi.org/10.1016/S0032-3861(01)00260-9)
- Naem, A., Saeed, B., AlMohamadi, H., Lee, M., Gilani, M. A., Nawaz, R., & Yasin, M. (2024). Sustainable and green membranes for chemical separations: A review. *Separation and Purification Technology*, 336, Article 126271. <https://doi.org/10.1016/j.seppur.2024.126271>
- Nilsson, R., Olsson, M., Westman, G., Matic, A., & Larsson, A. (2022). Screening of hydrogen bonds in modified cellulose acetates with alkyl chain substitutions. *Carbohydrate Polymers*, 285, Article 119188. <https://doi.org/10.1016/j.carbpol.2022.119188>
- Nilsson, R., Özeren, H. D., Putra, O. D., Hedenqvist, M., & Larsson, A. (2023). Experimental and simulated distribution and interaction of water in cellulose esters with alkyl chain substitutions. *Carbohydrate Polymers*, 306, Article 120616. <https://doi.org/10.1016/j.carbpol.2023.120616>
- Nunes, S. P., Culfaz-Emecen, P. Z., Ramon, G. Z., Visser, T., Koops, G. H., Jin, W., & Ulbricht, M. (2020). Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes. *Journal of Membrane Science*, 598, Article 117761. <https://doi.org/10.1016/j.memsci.2019.117761>
- Ogawa, K., Okamura, K., & Sarko, A. (1981). Molecular and crystal structure of the regenerated form of (1–3)- α -D-glucan. *International Journal of Biological Macromolecules*, 3(1), 31–36. [https://doi.org/10.1016/0141-8130\(81\)90021-0](https://doi.org/10.1016/0141-8130(81)90021-0)
- Ong, R. C., Chung, T.-S., Helmer, B. J., & De Wit, J. S. (2013). Characteristics of water and salt transport, free volume and their relationship with the functional groups of novel cellulose esters. *Polymer*, 54(17), 4560–4569. <https://doi.org/10.1016/j.polymer.2013.06.043>
- Papchenko, K., Degli Esposti, M., Minelli, M., Fabbri, P., Morselli, D., & De Angelis, M. G. (2022). New sustainable routes for gas separation membranes: The properties of poly (hydroxybutyrate-co-hydroxyvalerate) cast from green solvents. *Journal of Membrane Science*, 660, Article 120847. <https://doi.org/10.1016/j.memsci.2022.120847>
- Papchenko, K., Kentish, S., & De Angelis, M. G. (2025). An assessment of anion exchange membranes for CO₂ capture processes: A focus on Fumasep® and Sustainion®. *Polymers*, 17(11), 1581. <https://doi.org/10.3390/polym17111581>
- Papchenko, K., Ricci, E., & De Angelis, M. G. (2023). Modelling across multiple scales to design biopolymer membranes for sustainable gas separations: I—Atomistic approach. *Polymers*, 15(7), 1805. <https://doi.org/10.3390/polym15071805>
- Pasquini, D., Belgacem, M. N., Gandini, A., & Curvelo, A. A. D. S. (2006). Surface esterification of cellulose fibers: Characterization by DRIFT and contact angle measurements. *Journal of Colloid and Interface Science*, 295(1), 79–83. <https://doi.org/10.1016/j.jcis.2005.07.074>
- Peake, L. (2020). Plastic waste in the United Kingdom. In *Plastic waste and recycling* (pp. 585–600). Elsevier. <https://doi.org/10.1016/B978-0-12-817880-5.00023-2>
- Puanglek, S., Kimura, S., Enomoto-Rogers, Y., Kabe, T., Yoshida, M., Wada, M., & Iwata, T. (2016). In vitro synthesis of linear α -1,3-glucan and chemical modification to ester derivatives exhibiting outstanding thermal properties. *Scientific Reports*, 6(1), Article 30479. <https://doi.org/10.1038/srep30479>
- Puanglek, S., Kimura, S., & Iwata, T. (2017). Thermal and mechanical properties of tailor-made unbranched α -1,3-glucan esters with various carboxylic acid chain length. *Carbohydrate Polymers*, 169, 245–254. <https://doi.org/10.1016/j.carbpol.2017.04.015>
- Puleo, A. C., Paul, D. R., & Kelley, S. S. (1989). The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate. *Journal of Membrane Science*, 47(3), 301–332. [https://doi.org/10.1016/S0376-7388\(00\)83083-5](https://doi.org/10.1016/S0376-7388(00)83083-5)
- Pyo, S.-H., Park, J. H., Chang, T.-S., & Hatti-Kaul, R. (2017). Dimethyl carbonate as a green chemical. *Current Opinion in Green and Sustainable Chemistry*, 5, 61–66. <https://doi.org/10.1016/j.cogsc.2017.03.012>
- Ricci, E., Di Maio, E., Degli Esposti, M., Liu, L., Mensitieri, G., Fabbri, P., ... De Angelis, M. G. (2021). Towards a systematic determination of multicomponent gas separation with membranes: The case of CO₂/CH₄ in cellulose acetates. *Journal of*

- Membrane Science, 628, Article 119226. <https://doi.org/10.1016/j.memsci.2021.119226>
- Robeson, L. M. (2008). The upper bound revisited. *Journal of Membrane Science*, 320(1–2), 390–400. <https://doi.org/10.1016/j.memsci.2008.04.030>
- Robeson, L. M., Freeman, B. D., Paul, D. R., & Rowe, B. W. (2009). An empirical correlation of gas permeability and permselectivity in polymers and its theoretical basis. *Journal of Membrane Science*, 341(1–2), 178–185. <https://doi.org/10.1016/j.memsci.2009.06.005>
- Robeson, L. M., Smith, Z. P., Freeman, B. D., & Paul, D. R. (2014). Contributions of diffusion and solubility selectivity to the upper bound analysis for glassy gas separation membranes. *Journal of Membrane Science*, 453, 71–83. <https://doi.org/10.1016/j.memsci.2013.10.066>
- Russo, F., Galiano, F., Iulianelli, A., Basile, A., & Figoli, A. (2021). Biopolymers for sustainable membranes in CO₂ separation: A review. *Fuel Processing Technology*, 213, Article 106643. <https://doi.org/10.1016/j.fuproc.2020.106643>
- Sealey, J. E., Samaranayake, G., Todd, J. G., & Glasser, W. G. (1996). Novel cellulose derivatives. IV. Preparation and thermal analysis of waxy esters of cellulose. *Journal of Polymer Science Part B: Polymer Physics*, 34(9), 1613–1620. [https://doi.org/10.1002/\(SICI\)1099-0488\(19960715\)34:9<1613::AID-POLB10>3.0.CO;2-A](https://doi.org/10.1002/(SICI)1099-0488(19960715)34:9<1613::AID-POLB10>3.0.CO;2-A)
- Seidi, F., Arabi Shamsabadi, A., Ebadi Amooghin, A., Saeb, M. R., Xiao, H., Jin, Y., & Rezakazemi, M. (2022). Biopolymer-based membranes from polysaccharides for CO₂ separation: A review. *Environmental Chemistry Letters*, 20(2), 1083–1128. <https://doi.org/10.1007/s10311-021-01349-x>
- Seidi, F., Yazdi, M. K., Jouyandeh, M., Habibzadeh, S., Munir, M. T., Vahabi, H., ... Saeb, M. R. (2022). Crystalline polysaccharides: A review. *Carbohydrate Polymers*, 275, Article 118624. <https://doi.org/10.1016/j.carbpol.2021.118624>
- Sheppard, S. E., & Newsome, P. T. (1935). Some properties of cellulose esters of homologous fatty acids. *The Journal of Physical Chemistry*, 39(1), 143–152. <https://doi.org/10.1021/j150361a011>
- Simon, M., Fulchiron, R., & Gouanvé, F. (2022). Water sorption and mechanical properties of cellulosic derivative fibers. *Polymers*, 14(14), 2836. <https://doi.org/10.3390/polym14142836>
- Siparsky, G. L., Voorhees, K. J., Dorgan, J. R., & Schilling, K. (1997). Water transport in polylactic acid (PLA), PLA/ polycaprolactone copolymers, and PLA/polyethylene glycol blends. *Journal of Environmental Polymer Degradation*, 5(3), 125–136. <https://doi.org/10.1007/BF02763656>
- Siracusa, V., Rocculi, P., Romani, S., & Rosa, M. D. (2008). Biodegradable polymers for food packaging: A review. *Trends in Food Science & Technology*, 19(12), 634–643. <https://doi.org/10.1016/j.tifs.2008.07.003>
- Smith, Z. P., Hernández, G., Gleason, K. L., Anand, A., Doherty, C. M., Konstas, K., ... Freeman, B. D. (2015). Effect of polymer structure on gas transport properties of selected aromatic polyimides, polyamides and TR polymers. *Journal of Membrane Science*, 493, 766–781. <https://doi.org/10.1016/j.memsci.2015.06.032>
- Sun, C. C. (2008). Mechanism of moisture induced variations in true density and compaction properties of microcrystalline cellulose. *International Journal of Pharmaceutics*, 346(1–2), 93–101. <https://doi.org/10.1016/j.ijpharm.2007.06.017>
- Taylor, J. R. (1997). *An introduction to error analysis: The study of uncertainties in physical measurements* (2. ed.). University Science Books.
- Vane, L. M. (2016). Separations versus sustainability. In *Sustainability in the design, synthesis and analysis of chemical engineering processes* (pp. 35–65). Elsevier. <https://doi.org/10.1016/B978-0-12-802032-6.00002-5>
- Vatanpour, V., Yavuzturk Gul, B., Zeytuncu, B., Korkut, S., İlyasoğlu, G., Turken, T., ... Saeb, M. R. (2022). Polysaccharides in fabrication of membranes: A review. *Carbohydrate Polymers*, 281, Article 119041. <https://doi.org/10.1016/j.carbpol.2021.119041>
- Vieira, M. G. A., Da Silva, M. A., Dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal*, 47(3), 254–263. <https://doi.org/10.1016/j.eurpolymj.2010.12.011>
- Wijmans, J. G.(H.), & Baker, R. W. (2006). The solution-diffusion model: A unified approach to membrane permeation. In Y. Yampolskii, I. Pinnau, & B. Freeman (Eds.), *Materials science of membranes for gas and vapor separation* (1st ed., pp. 159–189). Wiley. <https://doi.org/10.1002/047002903X.ch5>
- Wijmans, J. G., & Baker, R. W. (1995). The solution-diffusion model: A review. *Journal of Membrane Science*, 107(1–2), 1–21. [https://doi.org/10.1016/0376-7388\(95\)00102-1](https://doi.org/10.1016/0376-7388(95)00102-1)
- Willberg-Keyriläinen, P., Vartiainen, J., Harlin, A., & Ropponen, J. (2017). The effect of side-chain length of cellulose fatty acid esters on their thermal, barrier and mechanical properties. *Cellulose*, 24(2), 505–517. <https://doi.org/10.1007/s10570-016-1165-x>
- Wohlert, M., Benselfelt, T., Wågberg, L., Furó, I., Berglund, L. A., & Wohlert, J. (2022). Cellulose and the role of hydrogen bonds: Not in charge of everything. *Cellulose*, 29(1), 1–23. <https://doi.org/10.1007/s10570-021-04325-4>
- Wu, F., Misra, M., & Mohanty, A. K. (2021). Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging. *Progress in Polymer Science*, 117, Article 101395. <https://doi.org/10.1016/j.progpolymsci.2021.101395>