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The use of biobased polymeric materials as membrane technologies for CO_2 capture and separation: a review

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ABSTRACT

Bio-based polymers have recently emerged as a promising alternative to conventional materials for carbon dioxide (CO_2) separation, offering a sustainable and environmentally friendly approach to mitigating greenhouse gas emissions. This review explores recent advancements in the design and application of bio-based polymeric membranes for CO_2 capture, focusing on their structural properties, separation performance, and scalability. The unique characteristics of bio-based polymers, including tunable functional groups, high processability, and biocompatibility, make them highly suitable for selective CO_2 separation in various industrial applications, provided that key challenges such as improving permeability-selectivity trade-off and enhancing chemical stability under harsh conditions, are properly addressed. Additionally, the integration of bio-based polymers with other advanced materials, including nanocomposites and hybrid membranes, is examined as a strategy to further enhance separation efficiency. This review provides a comprehensive overview of the current state of bio-based polymers in membrane technologies for CO_2 separation, highlighting both their potential and the technical challenges that need to be addressed for large-scale implementation.

1. Introduction

It is difficult to imagine a world without plastics or synthetic polymers today, since they have been thriving in global industries over the past 60 years because of their adaptability, durability and price [1]. Polymers, and synthetic polymers in particular, are crucial to modern society, especially in markets such as packaging, automotive, textile, electronics, but they come with significant environmental costs. The production of plastics is energy-intensive and heavily relies on fossil fuels like oil and natural gas. As a consequence, as shown in Fig. 1, synthetic plastic emits huge amounts of greenhouse gas (GHG) in all step of their life [2].

Studies suggest that the plastic industry accounts for about 6 % of global oil consumption, and by 2050, plastics could account for up to 20 % of oil demand. The production and incineration of plastics emit over 850 million tons of greenhouse gases annually, which could increase to 2.8 billion tons by 2050 [3].

The manufacturing process releases large quantities of carbon dioxide (CO_2) and methane (CH_4), both potent greenhouse gases (GHG) and their disposal contribute to global warming too as the majority of monomers used to make plastics, such as polyethylene, polystyrene and polypropylene, are not biodegradable [4]. Plastic waste, in fact, degrades very slowly and, when they are dispersed into landfills or in the ocean, they are reduced to microplastics and accumulate, thus releasing methane into the atmosphere, or disrupting entire ecosystems [5,6]. On the other hand, when plastics are incinerated for waste management, they release greenhouse and harmful gases such as CO_2, carbon monoxide (CO), and toxic chemicals like dioxins, which contribute to air pollution and global warming [7].

The global CO_2 emission, currently estimated in more than 36 billion tons/year, contributes greatly to the accumulation of so-called greenhouse gases (GHGs) in the atmosphere, which trap heat and block outward radiation [8,9]. Its alarmingly increasing levels (from its preindustrial baseline of approximately 280 ppm to around 408 ppm in recent years [10]) are therefore considered as one of the main driver of climate change and global warming which are causing today serious environmental problems [11,12].

Addressing these impacts requires innovation in bio-based alternatives, recycling technologies, and better waste management practices to mitigate the long-term effects of polymer use on the environment and to meet the needs of people living today without compromising the needs and wellness of future generations [13].

To facilitate the transition to more sustainable polymers, research

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List of abbreviations

[EMIM][Ac]	1-ethyl-3-methylimidazolium acetate
AEAPTMSP	3-(2-Aminoethylamino) propyltrimethoxysilane
BCP	Block copolymer material
BECCS	Bioenergy with carbon capture and storage
Bio-PE	bio-polyethylene
Bio-PET	Bio-poly(ethylene terephthalate)
Bio-PP	Bio-polypropylene
BNC	Bacterial nanocellulose
CA	Cellulose acetate
CDA	Cellulose diacetate
CCS	Carbon Capture and Storage
cm-Chitosan	Carboxymethylated chitosan
cm-CNF	Carboxymethylated cellulose nanofibrils
CMC	Carboxymethylated cellulose
CNC	Cellulose nanocrystals
CNF	Cellulose nanofibrils
CNT	Carbon nanotube
CS	Chitosan
CTA	Cellulose triacetate
DS	Degree of acetylation
EC	Ethyl cellulose
FTM	Facilitated transport membranes
GHG	Greenhouse gases
GNP	Graphene nanoparticle
GO	Graphene oxide
HPEI	Hyperbranched polyethyleneimine
HT	Hydrotalcite
IL:	Ionic liquid
IPCC	Intergovernmental Panel of Climate Change
Lignin (SW)	Softwood Lignin
Lup:	Lupamin
MFC	Microfibrillated cellulose
MOF	Metal-organic frameworks
MWCNT	Multi-walled carbon nanotube
MWCNT-β-CD	Multi-walled carbon nanotube functionalized with β cyclodextrin
NFC	Nanofibrillar cellulose
PAMAM	Polyamidoamine
PBT	Poly(butylene terephthalate)
PEBA	poly(ether-block-amide)
PEG	Polyethylene glycol
PEI	Polyethyleneimine
PEO	Poly(ethylene oxide)
PES	Poly(ether sulfone)
PESF	Poly(ether-sulfone)
PHA	Polyhydroxyalkanoate
PIM	Polymer of intrinsic microporosity
PLA	Poly lactic acid
PM or PI	Polyimine
PPG	Polypropylene glycol
PU	Polyurethane
PVAm	Polyvinyl amine
PVA	Poly vinyl alcohol
PZ	Piperazine
SF	Silk fibroin
SHPAA	sterically hindered polyallylamine
TPS	Thermoplastic starch
UiO-66-NH_2	Amine-functionalized Zirconium-based metal-organic framework
ZIF	Zeolitic imidazolate framework

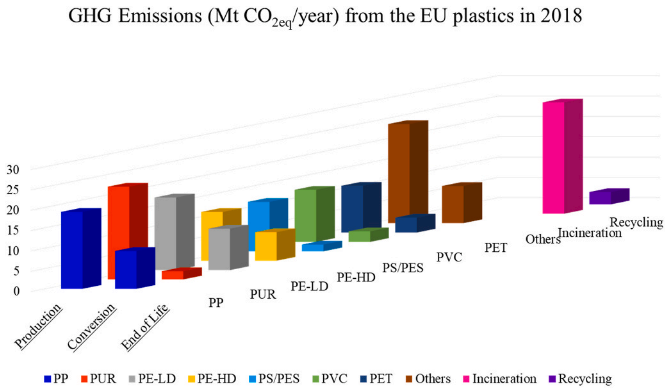

Fig. 1. Estimated total annual greenhouse gas emissions from EU and global plastics value chains reworked from reference [2].

efforts have long focused on converting bio-feedstocks into compounds identical to those derived from petroleum [14] as well as on producing new polymeric materials obtained from renewable resources that can be processed to engineer plastic-like products of desired structural and functional properties for applications [15].

The latter bio-based polymers, which can be either biodegradable or not, are derived from renewable resources like chitosan, cellulose, and starch, and can reduce the environmental footprint by reducing our reliance on finite fossil fuels [16]. This necessitates the attainment of physico-chemical properties and mechanical performance attributes—including flexibility, brittleness, and rigidity—that are analogous to those found in conventional plastics [14].

In present years biopolymers are a reality which is slowly entering the market. Many renewable materials are today used in packaging applications [17–19] and there has been an increase in the use of biopolymer-blended materials in composites because of their desirable characteristics as a renewable material reinforced by growing environmental concerns [4,14,20]Currently, the most significant bio-based polymers in terms of production volume are poly lactic acid (PLA), starch-based plastics and cellulose acetate (CA) materials [18,21–24]. However, the prevailing trend aims to promote and expand the global production capacity of various types of bio-based plastics [25]. As an example, bio-based polymers analogous to petroleum-derived ones, such as bio-polyethylene (Bio-PE), bio-polypropylene (Bio-PP), and bio-poly (ethylene terephthalate) (Bio-PET) have known an increasing interest as sustainable alternatives to conventional polymers in packaging applications [19]. On the same line, Bio-PU was indicated as possible substitute in foam for footwear, packing and biomedical applications and in functional textiles, thanks to possibility to produce electrospun nanofibrous membranes with promising features [26]. This is, however, not the only output of bio-based polymers since these renewable materials can be used in a wide variety of applications such as fabric industries, drug delivery, pharmaceutical technologies and as membranes for carbon capture [10,27–29].

Carbon capture, in particular, has been broadly studied worldwide in recent years since it could represent the quicker and more straightforward solution to limit climate change [30–32]. In order to meet the 1.5 °C temperature increase limit set by the Intergovernmental Panel of Climate Change (IPCC) in 2018 [33], it has therefore become imperative to develop and implement novel strategies to limit CO_2 emissions arising from combustion of fossil fuels, including Carbon Capture and Storage (CCS) system [34–36].

Membrane technology, in this concern, is an innovative method for gas separation with respect to more classical technologies such as absorption and adsorption, as its industrial applications started only in the second half of the last century [37]. Membranes can optimize the gas separation process by (i) reducing the equipment size and the capital costs, (ii) improving the process safety and operational simplicity, thanks to the absence of complex control systems, and (iii) lowering energy requirement, especially when pressurized gas is already available [31,32,38].

Polymers have taken the spotlight among the various membrane materials for gas separation because they present a compact configuration, a large-scale reproducibility, and low material and manufacturing cost [37]. Polymeric materials offer indeed several advantages, including solution-processability and precise control over chemical functionality. In this regard, bio-based polymers have gained an increasing interest as an alternative material for membrane development, offering unique advantages such as sustainability, biodegradability, and tunable properties.

The present review summarizes some of the most interesting current trends in biobased polymeric research for membrane separation. Following this line of thought, studies about gas transport properties of self-standing and hybrid films of commercial bio-based materials have been investigated for CO_2/N_2, CO_2/CH_4 and H_2/CO_2 separation, as reported in the following sections of this work, to understand their separation properties for carbon capture applications [18,23,24].

The focus is primarily on biodegradable biobased polymers, which promise a lower end of life issues with respect to their synthetic counterparts. In particular, recent advancements involving nanocellulose and chitosan-based membranes will be taken into account, considering both as pure materials and as composites, often enhanced with different fillers to improve transport properties and CO_2 separation efficiency. On the other hand, it was decided not to analyze in detail the case of cellulose acetates as the extensive body of literature existing on these polymeric membranes suggests that they are well-explored due to their excellent film-forming ability, high chemical and mechanical stability, and in general excellent gas separation properties, which makes them still today an ideal candidate for gas separation applications, as presented below in Table 1 [23,86].

In this review, therefore, the fundamentals of gas transport in polymers and the benchmark performance of conventional petroleum-derived membranes are first briefly recalled. The attention then moves to bio-based and biodegradable polymers, with discussion of their chemical characteristics, advantages and limitations with respect to synthetic analogues, followed by a critical examination of the available literature concerning membranes produced from such materials. The present work aims, indeed, at exploring new and potentially innovative bio-based membrane to go beyond the established research and explores newer materials that hold promises for improving separation performance, particularly in the context of carbon capture.

In this concern, it should be noted that in this review advancement related to biopolymers ability to obtain enhanced cost-efficiency, environmental sustainability with respect to fossil fuel-based plastics, will be considered only in a qualitatively literature-based sense: the primary focus remains on gas-transport performance (permeability and selectivity) and not on detailed techno-economic analysis or scalability and sustainability assessments.

2. Mass transport in polymers for gas separation

2.1. Solution diffusion membranes

In recent years, membranes and polymeric membranes in particular, have become more and more of interest in gas separation with particular reference to applications related to CO_2 purification, due to the increasing interest for carbon capture. The low energy consumption and intrinsic simplicity of the process indeed make it particularly appealing for this kind of application provided that more performing materials and modules become available [37,87–90].

Gas separation with polymeric membranes is a pressure-driven process, where a gas is flown on a thin selective layer that has the ability to separate different chemical species according to their different size and interactions with the material [91]. For dense, non-porous membrane, the transport is usually governed by solution-diffusion mechanism, through which each component in the gas feed dissolves in the membrane polymer at its upstream surface and then diffuses through the polymer layer along a chemical potential gradient to the opposite side where they emerge into the downstream gas phase [92]. Accordingly, the permeation rate depends on thermodynamics factors (partitioning of species between feed phase and membrane phase), kinetics properties (diffusivity, D), thickness of the selective layer, and the interaction between the polymer and the penetrant [37,93]. In this concern, membrane material and structure have an important role in determining the suitable materials for gas separation membranes: resistance, durability, pores, channels formations (which exhibit diverse sizes and topologies) and polymer's free volume (the "unoccupied" space between the polymeric chains) directly influence the transport properties of low molecular weight species and gases [37,94,95].

The separation performance of polymeric membranes is described by two key parameters: permeability (P) and selectivity (α). Permeability is the rate at which any compound permeates through a membrane, while selectivity is the ability of a membrane to accomplish a given separation and to achieve high product purity and high recovery [96,97]. Permeability is generally defined as follows, through its relationship with permeation flux:

$$J_i = -\frac{P_i\left(p_i^{up} - p_i^{down}\right)}{l} \tag{1}$$

Where J_i is the molar flow per unit surface of the ith component across the membrane, l is the membrane thickness, $(p_i^{up} - p_i^{down})$ is the partial pressure difference of the ith component through the membrane (*up* for upstream and *down* for downstream).

On the other hand, the separation capability of a membrane, by means its selectivity respect to a gas mixture can be determined as reported in Eq. (2):

$$\propto_{i/j} = \frac{y_i^{down} \Big/ y_j^{down}}{y_i^{up} \Big/ y_j^{up}} \approx \left(\frac{P_i}{P_j}\right) \tag{2}$$

where the y refers to the molar fraction of the components of interest (i or j) at the two sides of the membrane and can be approximated to the ratio of components permeability for pure gas measurements, when the downstream pressure is close to zero (ideal selectivity).

Since permeability is an intrinsic material property, gas flux can be enhanced by minimizing membrane thickness to submicron scale, by using porous support to sustain mechanical stress related to pressure gradients across the membrane.

In industrial applications, achieving high gas flux is often prioritized over selectivity, highlighting the importance of fabricating membranes with minimal thickness [98]. Performance is typically assessed using permeance, which accounts for the permeability relative to the membrane's thickness. The most common units used are Barrer for permeability and gas permeance units (GPU) for permeance, represented in SI units as follows:

$$1\ Barrer = 7.5\ .\ 10^{-18}\frac{m^3(STP).m}{m^2.s.Pa} = 10^{-10}\frac{cm^3(STP).cm}{cm^2.s.cmHg}$$

$$1\ GPU = 7.5\ .\ 10^{-12}\frac{m^3(STP)}{m^2.s.Pa} = 10^{-6}\frac{cm^3(STP)}{cm^2.s.cmHg} = \frac{barrer}{\mu m}$$

Achieving the right balance between permeability and selectivity is essential for maximizing membrane performance, ensuring high product purity, and enabling efficient gas recovery. As noted by Robeson [87,96,

Table 1
Separation properties for biobased polymeric membranes.

Membrane		Temperature	Feed Pressure	Thickness	CO_2 Permeability	Selectivity			Ref.
Biopolymer	Additive	*°C*	*bar*	*μm*	*Barrer*	CO_2/N_2	H_2/CO_2	CO_2/CH_4	
CA (DS1.75)	–	35	1	3000 to 5000	1.84	32.3	–	35.6	[39]
CA (DS2.84)	–	35	1	3000 to 5000	6.56	28.52	–	32.8	
CDA	–	35	7.5	50–60	6.15	–	–	30.4	[40]
CTA	–	35	7.5	50–60	6.51	–	–	25.3	
Swollen CDA	–	35	7.5	50–60	5.31	–	–	24.5	
Swollen CTA	–	35	7.5	50–60	5.46	–	–	22.7	
CA	ZIF-62 glass nanoparticles (2-12 wt %)	25	3	60-65[d]	15.8 to 84.8	–	–	12.2 to 35.3	[41]
CA	Co^{2+}-Sodium ZeoliteY (15 wt %)	25	2 to 10	30	2.5 to 3.5	25 to 35	–	–	[42]
CA	CNT	25	2	30 to 40[d]	3.41 to 7.76	7.75 to 9.94	–	12.72 to 16.23	[43]
CA	Carboxylated CNT	25	2	30 to 40[d]	6.53 to 14.21	13.60 to 16.8	–	21 to 21.81	
CA	MWCNT	25	1 to 3	N/A	–	5.5	–	–	[44]
CA	MWCNT-β CD	25	1 to 3	N/A	–	39.5 to 40	–	–	
CA	Silica (5-20 wt %)	25	10	40 to 60[d]	6.32 to 7.3	32 to 80	–	–	[45]
CA	Pebax (2–8 wt %)	25	2	N/A	2.2 to 2.7	19 to 29	–	–	[46]
CA	Pebax (8 wt %)	25	2 to 10	N/A	2.3 to 2.7	24 to 29	–	–	
CA	PM-4 (3 wt %)	35	3	115	3000	59	–	33.7	[47]
CTA	NH_2-ZIF-8 (10 wt %)	N/A	4	24.77	218	13.84	–	–	[48]
EC	–	25	2	24.77	67.7	21.3	–	11.1	[49]
	–	55	2	24.77	90	21.8	–	6.97	
EC	GO (1.1 wt %)	25	2	50	75	30	–	–	[50]
EC	ZIF-8/GO (20 wt %)	25	2	50	203	33	–	–	
CNF	–	35	1	20	0.5 to 18	520 to 610	–	265 to 420	[51]
Lup+50 %CNF	–	35	1	20	0.85 to 190	50 to 210	–	25 to 75	
CNF	–	35	1	50	5 to 126	64 to 225	–	265 to 420	[52]
Lup/CNF (30:70 wt %)	–	35	1	50	7 to 77	30 to 136	–	20 to 100	
Lup/CNF (70:30 wt %)	–	35	1	50	70 to 213	85 to 220	–	30 to 135	
cm-CNF	–	35	1	15 to 20[d]	3 to 30	26 to 55	–	–	[53]
cm-CNF	L-Arginine (15 wt%)	35	1	35 to 45[d]	5 to 60	7 to 17	–	–	
cm-CNF	L-Arginine (30 wt %)	35	1	35 to 45	75 to 225	38 to 40	–	–	
cm-CNF	L-Arginine (45 wt %)	35	1	35 to 45	70 to 230	75 to 190	–	–	
cm-CNF	PVAm	35	1	50 to 60[d]	160	20	–	10	[54]
	PVAm + Arginine (25 wt %)	35	1	50 to 60	250	50	–	–	
	PVAm + Arginine (45 wt %)	35	1	50 to 60	340	45	–	20	
cm-CNF	–	40	1.5	23.3 ± 2.8	3 to 40	25 to 56	–	–	[55]
	PVAm	40	1.5	35.5 ± 3.2	10 to 50	20 to 71	–	–	
	PVAm-AEAPTMSP	40	1.5	34.7 ± 3.5	20 to 92	40 to 131	–	–	
CNF	[EMIM][Ac] (20 wt %)	35	1	50	2 to 155	35 to 127	–	–	[56]
	[EMIM][Ac] (35 wt %)	35	1	50	6 to 300	54 to 370	–	–	
	[EMIM][Ac] (50 wt %)	35	1	2	60 to 330	60 to 98	–	–	
Tunicate CNF	Starch+5 %Lignin (SW)	25	0	2	59.8	1315	1.2	–	[57]
Tunicate CNF	Starch	25	0	2	2.6	96	1	–	
CNF	ZIF-8 (70 wt %)	25	3	N/A	550	45.5	–	36.2	[58]
CNF	UiO-66-NH2	25	N/A	N/A	139		46		[59]
PVAm	CNC (10 wt %)	35	1.7	0.2	69[b]	50	–	–	[60]
	CNF (10 wt %)+β-alanine	35	1.7	0.2	52.6[b]	50	–	–	
PVA	CNC (80 wt %)	25	2	0.2	671.95	43.6	–	–	[61]
	CNF (80 wt %)	25	2	0.2	470.79	34.57	–	–	
PVA	CNC (1 wt %)	N/A	5	0.9	96.3[b]	–		43	[62]
PVA	CNC-low charge (4 wt %)	23	1.2	0.89	92.6	37.5	–	–	[63]
	CNC-high charge (4 wt	23	1.2	0.89	90.7	42	–	–	
	CNC-phosphrylated (4 wt %)	23	1.2	0.89	100	42	–	–	
	CNC (4 wt %)	23	1.2	0.89	128	39	–	–	
	CNF-high charge (10 wt %)	23	1.2	0.89	117	36	–	–	
PVA	Phosphorylated CNF (10 wt %)	25	1.2	0.82	77	42	–	–	[64]
	Phosphorylated CNF-high charge (10 wt %)	25	1.2	0.82	100	50	–	–	
	Phosphorylated CNF-high charge-screened (10 wt %)	25	1.2	0.82	117	46	–	–	
PVA/L-Arginine	Phosphorylated-CNC (1 wt %)	23	1	0.85	21177	–	–	33	[65]
	Phosphorylated -CNC (2 wt %)	23	1	5	25772	–	–	10	
PVA/L-Arginine	cm-CNC (1 wt %)	23	1	1.88	11705	–	–	19	[66]
Pebax 1675	CNC (5 wt %)	25	2	1.88	305.7	41.6	–	–	[67]
PEBA	CNC (1 wt %)	25	4	1	7.10 ± 5.2	53.2 ± 5.4	–	–	[68]
PU	CNC (1 wt %)	25	4	1	6.233 ± 4.5	48.1 ± 4.4	–	–	[68]

(*continued on next page*)

Table 1 (*continued*)

Membrane		Temperature	Feed Pressure	Thickness	CO_2 Permeability	Selectivity			Ref.
Biopolymer	Additive	°*C*	*bar*	*μm*	*Barrer*	CO_2/N_2	H_2/CO_2	CO_2/CH_4	
Chitosan	–	22	2.53[a]	17	3 to 10	55 to 75	–	–	[69]
Chitosan		20 to 110	0.5	65	213 to 483	69 to 250	19 to 43	–	[70]
	–	150	0.5	65	399	194	29	–	
	–	20 to 150	4	65	156 to 286	150 to 131	12 to 17	–	
Chitosan	Na Alginate	20 to 150	1.5 to 5	65	1050 to 1500	630 to 730	45 to 133	–	[71]
cm-Chitosan	–	80 to 90	2	3	30 to 40	40 to 50	–	–	[72]
cm-Chitosan	PZ (20 wt %)	80	2	3	216[b]	102	–	–	
cm-Chitosan	PAMAM (10 wt %)	90	0.8[a]	2 to 3	254.8[b]	149	–	–	[73]
		60 to 110	0.8[a]	2 to 3	81.5 to 253[b]	51 to 145	–	–	
cm-Chitosan	PAMAM + HT (10 wt %)	90	2	1	123[b]	67	–	–	[74]
		60 to 110	2	1	67 to 123[b]	39 to 67	–	–	
cm-Chitosan	PEI (30 wt %)	30	0.2	16	10080[b]	325	–	–	[75]
Chitosan	SF + GNP	90	2	1	159[b]	93	–	–	[76]
		90	2	1	126[b]	104	52[c]	–	
Chitosan	GNP	90	2	1	46[b]	54	–	–	[76]
		90	2 to 5.91	1	27 to 46[b]	57 to 26	–	–	
Chitosan	[EMIM][Ac] (5 wt %)	25	0.5	N/A	1293	4.6	–	–	[77]
		50	0.5	N/A	1338	4.6	–	–	
Chitosan	L-tyrosine (grafted)	85	2.2	0.6	61.8[b]	31	–	–	[78]
		25 to 115	2.2	0.6	18 to 61.8[b]	9 to 31	–	–	
Chitosan	Phenylalanine-grafted (20 wt %)	85	2.21	4	424[b]	89	–	–	[79]
	Phenylalanine-blended (20 wt %)	85	2.21	4	288[b]	97	–	–	
Chitosan/PVAm	HPEI-GO (3 wt %)	25	1	3.5	112[b]	107	–	–	[80]
PLA Easy Fil-White	–	25	1 to 12	27	70	–	2	285	[81]
PLA (Nature Green 100D)	–	25	1	26	1	–	26.5	–	[82]
PLA (Nature Green 2100D)	–	25	1	26	11	–	–	221 to 231	[83]
PLA	–	25	0.2 to 09[a]	50 ± 2	1.12 ± 0.05	22.4	–	–	[84]
PES	Amino Starch (2 wt %)	20	27	N/A	2.89	–	–	61.2	[85]

[a] Pressure difference is considered.

[b] Permeability is calculated based on reported thickness and permeance.

[c] The selectivity reported is calculated for CO_2/H_2 based on a ternary ($CO_2/H_2/N_2$) mixed gas permeation test.

[d] Average value is considered for permeability.

99–101], polymeric membranes typically face a trade-off between these two parameters: increasing selectivity, indeed, often reduces permeability, and vice versa. The primary challenge in optimizing gas separation processes lies in overcoming this limitation, which is indeed crucial for enhancing both separation efficiency and practical application viability. To visualize this trade-off, Robeson introduced the concept of an upper bound, a benchmark that defines the empirical relationship between permeability and selectivity for various gas pairs in polymeric membranes. He established this by extensively surveying literature data and graphing the available permeability/selectivity combinations. First proposed in 1991 [101] and later revised in 2008 [102], this upper bound - which represent the performance frontier of a

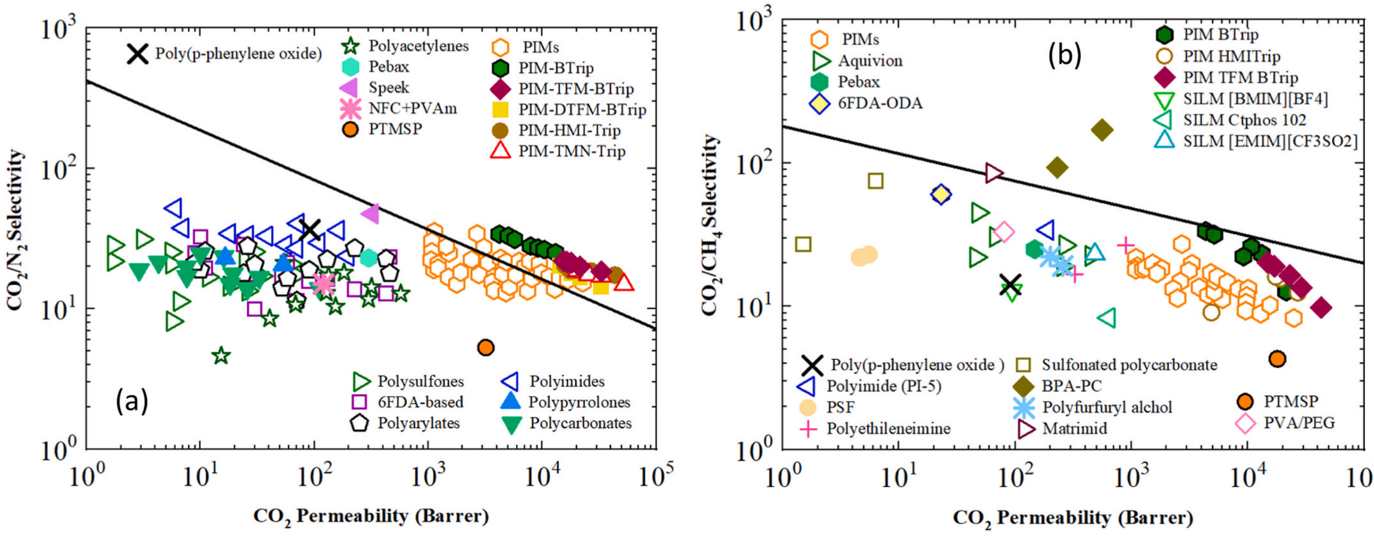

Fig. 2. Robeson Upper-bound plot from 2019 for (a) CO_2/N_2 [104–110]and (b) CO_2/CH_4 [104,111–116] gas pairs.

membrane, above which virtually no data points exist-is based on a log–log plot of α_{ij} versus P_i. Moreover, in 1999, Freeman provided a theoretical prediction supporting this empirical relationship, as expressed in Eq. (3):

$$\propto_{i/j} = \left(\frac{\beta_{i/j}}{P_i^{\lambda_{i/j}}}\right) \tag{3}$$

Based on the solution-diffusion mechanism, $\beta_{i/j}$ and $\lambda_{i/j}$ are empirical constant, in which the latter depends on the size of the penetrant gas molecules, suggesting that the slope of the upper bound is a natural consequence of the strong size-sieving nature characteristic of stiff-chain glassy polymeric materials [97,103].In 2019, updated upper bounds were specifically introduced for CO_2/CH_4 and CO_2/N_2 separations (Fig. 2), offering a more relevant benchmark for current materials and applications [104]. In this review, both the 2008 and 2019 upper bounds are used as reference points to evaluate the performance of bio-based membrane materials, with the goal of identifying systems that approach or surpass this established trade-off.

In these plots, each data point represents a membrane material, with the x-axis showing permeability and the y-axis selectivity; thus, optimal performance is achieved by shifting towards the top-right corner—indicating enhancement of both properties. Surpassing the upper bound is considered a key goal in membrane development, particularly for emerging materials like bio-based systems. It should be noted, however, that Robeson plots do not directly refer to thin film membranes usually considered in industrial separations. Optimal membranes, in real application, may result from different considerations related for example to pressure ratio available which may lead to the need of increasing permeability rather than selectivity of a membrane [117]. As an example, in post combustion carbon capture, where pressure differences are usually limited, commercial membranes focus on increasing permeability (even above 4000 GPU), while giving less attention to selectivity which typically remains in the range of 50–170 [118,119].

2.2. Facilitated transport membranes

Among the different strategies to obtain better performances, facilitated transport membranes (FTMs) are particularly promising in different separations. FTMs enhance selective permeation by combining conventional solute diffusion with a reversible chemical reaction mechanism. Unlike traditional solution–diffusion membranes, FTMs integrate a carrier-mediated pathway that significantly improves both flux and selectivity for specific target gases or vapors [120]. The mechanism involves two concurrent transport phenomena: (i) physical diffusion of the free solute across the membrane, and (ii) chemical diffusion via reversible complexation between the solute (A) and a mobile or fixed carrier (C) within the membrane phase (Eq. (4)). On the high-pressure (feed) side, the solute reversibly reacts with the carrier to form a transient complex (AC). This complex diffuses through the membrane and dissociates on the low-pressure (permeate) side, regenerating the carrier and releasing the solute while unbound solute molecules and non-reactive species permeate solely through Fickian diffusion [121]. This cycle effectively mimics absorption and desorption processes within a membrane matrix, enhancing mass transport efficiency.

$$A + C \leftrightarrow AC \tag{4}$$

The efficacy of this mechanism relies critically on the reaction kinetics, the selectivity of the carrier for the target species, and the reversibility of the binding. In most industrial processes, which involve CO_2, feed streams are saturated with water vapor; hence, CO_2 permeation will be exposed to a competitive sorption of water in the membranes. However, when facilitated transport occurs, the presence of water vapor causes an enhancement of the CO_2 transport through the membrane due to the reversible reaction between the carrier and CO_2 in the feed gas [122].

Most common solution for facilitated transport membranes in CO_2 separation is indeed based on the use of basic carriers such as amine groups which interact with acidic CO_2 by forming carbamate or carbonate ions [121,123–125]. Other approaches were however also considered based on the use of different additives such as amino acid, inorganic salts and mimic enzymes [71,126–128].

2.3. State of the art in CO_2 separation membranes

Materials currently used for the separation of CO_2 are indeed various, but commercial ones are usually well below the target suggested by Robeson upper bounds as performance alone is not sufficient to guarantee suitability for market deployment [87,99]. Indeed, in addition to high permeability and selectivity, polymeric membranes must also be durable and present high enough thermal and chemical stability under the operating conditions expected in the application environment, that means to be able to withstand different processes such as CO_2 plasticization or ageing, to maintain performance in the operative conditions for an extended period of time [102,129,130].

In fact, when membrane technologies are used in post-combustion Carbon Capture systems, CO_2 is captured from a flue gas mixture, consisting of mainly CO_2, N_2, and water vapor, produced after the combustion of hydrocarbons with temperature ranging between 50 and 200 °C and pressure up to 1.5 bar [131,132], while higher temperatures and pressures are expected when precombustion capture is considered, where CO_2 needs to be separated mainly from CO, H_2 and water vapor [133–135]. Finally, several applications of CO_2 separation are related to separation from methane in natural gas sweetening and biogas upgrading [136,137]. While not usually considered in CCS approaches, these processes have indeed a great importance as today natural gas treatment coupled with enhance oil recovery is likely the most common CCS application at industrial scale while biomethane production is gaining more and more interest in BECCS (Bioenergy with Carbon Capture and storage) solutions [117,138–141].

Gas separation membranes have been commercially proven to work in the sweetening of natural gas (removal of CO_2 and H_2S) and are commonly used for H_2 recovery in refineries [114,142–147].

In natural gas sweetening system, many polymeric membranes, both rubbery and glassy reported to have great separation factors [148]. Polyimide (PIs) are reported to have CO_2 permeabilities between 7 and 20 Barrer and CO_2/CH_4 selectivity comprises 58 to 102 [149–151], while Fluorinated polymer, i.e. PFSA, Hyflon, cytop, modified Teflon and ionic liquid PVDF membrane, showed CO_2 permeability laying from 32 to 250 Barrer and selectivity in the range of 9–38, depending on temperature and relative humidity present in the stream [152–157]. PDMS, on the other hand, presents CO_2 permeability of 3250 Barrer but low CO_2/CH_4 (about 3.4), on the contrary of poly lactic acid (PLA) which exhibited low CO_2 permeability (in the range of 11–13 Barrer) shows an extremely high selectivity, up to 220–230 [83].

H_2-selective polymeric membranes are largely studied for pre-combustion capture where fossil fuels are reformed into synthesis gas (syngas) first and then in high pressure CO_2 and H_2. Separation of these two components allows for the storage of CO_2, while H_2 can be used for a number of processes, such as power generation or chemical synthesis. In general, glassy polymeric membranes, which operate below the glass transition temperature [158] provide high H_2/CO_2 selectivity due to a larger void fraction within the polymeric matrix. In their review, Scholes et al. [159], reported a large number of H_2/CO_2 separation performances for membrane materials, such as Polybenzimidazole (PBI)/nano porous silicate mixed matrix with selectivity up to 45 [160], polybenzimidazole, with a selectivity of 20 and CO_2 permeability approximately of 0.65 Barrer at 200 °C [145], and Matrimid [161], which instead presented lower selectivity in the order of 4. Regarding instead CO_2-selective membrane in pre-combustion capture, rubbery polymer resulted to be the most performing materials, such as poly(ethylene oxide) [162] and PDMS [163], which reported CO_2 permeability of 17 Barrer and 3100 Barrer and CO_2/H_2 selectivity of 9.9 and 3.4, respectively, as well as chitosan membranes that, thanks to their facilitated transport mechanism, reported to have CO_2 permeability up to 482 Barrer and CO_2/H_2 selectivity of 43 [70,71]. The high temperature of the steam reforming process, however, usually limits the applicability of polymeric membranes for this application.

On the other hand, many works reported CO_2 separation data with respect to N_2 in view of applications in post combustion capture. Lasseuguette et al. [164], for example, characterized PIM-1 (polymer of Intrinsic Microporosity) membranes for CO_2/N_2 separations determining CO_2 permeability around 7000 Barrer and selectivity of 19, both for pure and mixture streams. In terms innovative materials, indeed, looking at Fig. 2a the upper bound is dominated by high free volume glassy polymers such as PIM, thermally rearranged materials or triptycene based polymers [104] which, while structurally diverse, achieve exceptional performance as a result of their rigid backbones that prevent efficient molecular packing [165,166]. As occurs for PTMSP (which has the highest free volume of hydrocarbon-based polymers [93,97], this high FFV allows for significantly enhanced gas permeability, although their backbone stiffness and their tendency toward premature aging, stem not from a radical shift in their ability to differentiate gas solubility [167–170]. This loss of the necessary size-sieving capability and a severe drop in selectivity make those types of material still far from industrial deployment.

Polyamides are also quite promising for this application due to their good CO_2 separations performances with respect to N_2 and to their inherent chemical, thermal and mechanical stability, although they are subjected to aging [171,172]. In this concern, Tsvigu et al. [173] reported CO_2 permeability in 6FDA –6FpDA polyimide in the range of 50–80 Barrer, depending on pressure, temperature and relative humidity, with selectivity changing accordingly from 20 to 40. Those performances were an improvement with respect to more classical polyamides such as Matrimid, whose permeability toward CO_2 is from 4 to 10 Barrer, although selectivity lies between 30 and 50 [174,175]. Moreover, as already observed for previous applications, membranes are often bonded together to create block copolymer materials (BCPs) to improve separation performances, such for Pebax (PA-PEO) which is highly permeable to CO_2 (350 Barrer and CO_2/N_2 of 24, as reported by Casadei et al. [176]), polystirene-poly ethylene oxide BCPs (CO_2 permeability 25 and CO_2/N_2 37.7 at 35 °C [177] and poly(ethylene oxide) poly(butylene terephthalate) (PEO-PBT) whose permeability at 25 °C changes between 30 and 200 according to the PEO volume fraction content in the material, and selectivity up to 150 [178].

Although membrane technology is inherently low-energy and considered environmentally benign during operation, most synthetic polymers are not [179]. Synthetic polymers (from PIMs, to polyamides, rubbers and fluoropolymers), coupled with molecular-level design and hybrid architecture, can surely achieve competitive CO_2/N_2 performance, still relies on petrochemical feedstocks and exhibits non-negligible environmental burdens in production and end-of-life management. Consequently, the next development step in the field is not only to enhance transport properties, but to do so within more sustainable material platforms. For this reason, interest in bio-based polymeric membranes has rapidly increased in order to maintain separation performance while improving the overall sustainability of carbon capture processes [180]. Biopolymers are indeed abundant and diverse, and they have reportedly exhibited immense potential for carbon capture even if they require further investigation for application on a commercial scale [180,181]On this basis, the following section focuses specifically on the use of bio-based materials in gas-separation membranes, highlighting how bio-based polymers can match or complement the performance of synthetic systems.

3. Bio-based materials for gas separation membrane

Building on the considerations above regarding sustainability limitations of synthetic polymers, a growing research trend explores bio-based materials as membrane matrices or functional additives for CO_2 capture to reduce the use of oil-based plastics and to increase the sustainability of the process.

Bio-based membranes present an eco-friendlier option and can be engineered to enhance CO_2 selectivity over other gases, such as nitrogen (N_2) and methane (CH_4) [182]. Nanocellulose, Chitin and chitosan, polysaccharides, lignin, poly lactic acid (PLA), polyhydroxyalkanoate (PHA) and thermoplastics starches (TPS) are just some examples of these groups. Plants, animals, and microbes can all be used to make bio-based biopolymers although not all of them are biodegradable [183]. In fact, even though PLA, PHA and TPS are made from renewable sources, they are only partially biodegradable, meaning they can only be destroyed under certain conditions [184].

These materials can be used to prepare not only self-standing membranes but also as fillers to increase CO_2 transport properties (i.e. facilitated transport) or membrane resistance. Gas separation using biomaterials such as PLA, chitosan and Nanocellulose, for example, can be highly improved by adding aminated moieties (such as PVAm), amino acids, lignin or ionic liquid fillers to the substrate material, thus obtaining a membrane with high CO_2 affinity that result in high permeability and high selectivity [51,53,185]. As a matter of fact, nanocellulose and chitosan can be used to prepare self-standing membrane with good mechanical properties, but thanks to their strong ability to form hydrogen bonding, they are also considered excellent reinforced nanofiller for polymeric materials [186,187].

Different studies reported a fast increase of gas transport rate and permeability in bio-based materials upon water exposure [51,53] thus allowing the achievement of high gas selectivity by controlling the evolution of the membrane characteristics from barrier to highly permeable.

In essence, the principal reason to utilize bio-based materials for membranes is because one can potentially exploit their high stiffness and mechanical resistance together with their high separation performances with respect to CO_2, especially in the presence of humidity, still ensuring sustainability, green chemistry and eco-efficiency of the process.

Among these biomaterials, cellulose and chitosan seem the most promising biopolymers because they are biodegradable and biobased. Moreover, they are among the most abundant polymers present in nature and can be obtained from waste, strengthening the idea of the circular economy.

3.1. Cellulose

Cellulose is the most abundant and renewable biopolymer on Earth extracted from plant cells. It is predominantly found in vascular plants, where it serves a critical structural role in the composition of plant cell walls. The chemical structure of this material consists of a linear homopolysaccharide consisting of β-(1 → 4)-linked D-glucose units (Fig. 3a). The isolation process plays a significant role on the material's structural characteristics, such as the degree of inter- and intra-molecular hydrogen bonding, chain length distribution, crystallinity, and the arrangement of functional groups along the polymer chains [188]. The hydrogen bonding network, both within and between cellulose chains, is considered the primary determinant of its physicochemical properties, including its crystallinity, mechanical strength, and chemical reactivity.

To exploit the structural benefits of cellulose more effectively, various derivatives have been developed through chemical modification or functionalization. Common derivatives of cellulose are obtained via acetylation, carboxymethylation and phosphorylation of this material. This category of cellulose-based materials is known for their enhanced

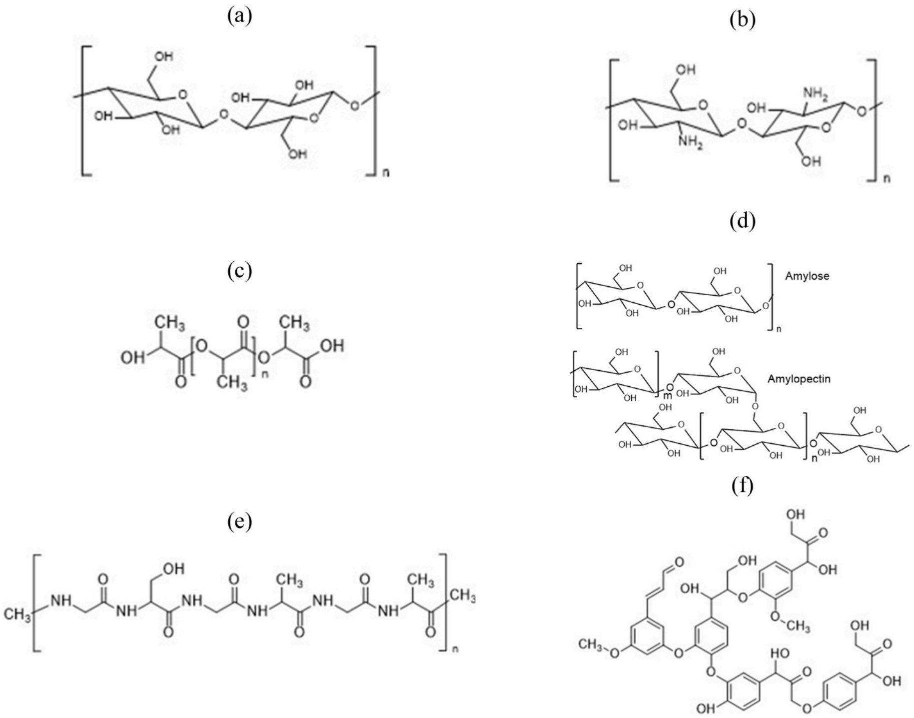

Fig. 3. Structure of Bio-based polymers (a) Cellulose, (b) Chitosan, (c) PLA, (d) Starch (made of Amylose and Amylopectin), (e) Silk Fibroin, (f) Lignin.

reactivity, improved stability and controllability as properties such their hygroscopic nature can be tuned accordingly [189,190]. Many commonly used cellulose derivatives, such as cellulose acetates (CA) and carboxymethyl cellulose (CMC), lack proper chemical and thermal stability which limits their operating range for gas separation applications; nonetheless they have been widely used and considered for membrane production [191,192].

Cellulose acetate (CA), a product of cellulose acetylation, is produced by substituting hydroxyl groups on the cellulose backbone with acetyl groups, identified by degree of substitution or degree of acetylation. Depending on the degree of substitution of cellulose, other derivatives such cellulose diacetate (CDA) and cellulose triacetate (CTA) can be obtained. In this cellulose derivative, water solubility is strongly influenced by the degree of substitution, decreasing significantly once the substitution level exceeds 0.5 —highlighting the critical role of substitution degree in determining its physicochemical properties [86,193].

The substitution of abundant hydroxyl groups on cellulose leads to the formation of carboxymethylated cellulose, thus modifying the characteristic properties of this material including its hydrophilicity, surface properties and mechanical strength [194,195].

Ethyl cellulose (EC) is another cellulose derivative that has been studied for gas separation application. This material is a product of replacing hydroxyl groups of cellulose with ethyl groups through a reaction with ethyl chloride. This derivative is characterized by its hydrophobicity and chemical stability [196].

Other cellulose derivatives have been widely investigated for their properties and applications, with several reviews on the topic [23,191,196–198]. Among them, nanocellulose has been extensively studied in recent years and identified as a promising bio-based alternative for gas separation.

Nanocellulose, a nanoscale form of cellulose, offers unique properties such as low density (around 1.6 g/cm^3), exceptional mechanical strength, a high aspect ratio, and an expansive surface area rich in hydroxyl functional groups. Due to its origin, nanocellulose also retains many of cellulose's inherent advantages, including renewability, biodegradability, hydrophilicity, low toxicity, and biocompatibility [199,200].

Nanocellulose is identified as a natural fiber with various hydroxyl groups and strong hydrogen bonding network creating a matrix of both crystalline and amorphous structure. [199,201]. On the downside, it can increase the chance of aggregation of these nanoparticles. This effect can be magnified with higher specific surface area and smaller particle size [202].

Nanocellulose can be classified into three main groups based on its shape and origin: cellulose nanocrystals (CNC), cellulose nanofibers (CNF), and bacterial nanocellulose (BNC). Each category is identified by different morphological characteristics and particle size depending on their source of origin and extraction method while sharing the same chemical composition as cellulose [201–203]. [201,203].

Cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) are two major forms of nanocellulose with distinct structures and production methods. CNCs are rod-shaped, highly crystalline nanoparticles (2–20 nm in diameter, 100–500 nm in length) obtained primarily through acid hydrolysis, which removes the amorphous regions of cellulose fibers [201]. Alternative methods include enzymatic hydrolysis, TEMPO oxidation, gaseous acid hydrolysis, and ionic liquid treatment [202]. CNFs, on the other hand, are long, flexible, and entangled fibrils (1–100 nm in diameter, 500–2000 nm in length) produced by mechanical delamination of cellulose fibers [200]. Due to the high energy demand of this process, pretreatment steps such as acid hydrolysis or enzymatic reactions are often used [202]. CNFs contain both crystalline and amorphous regions, with morphology and particle size depending on the processing conditions. They are commonly referred to as microfibrillated cellulose (MFC) and nanofibrillar cellulose (NFC) in the literature. Here, the term CNF is used to refer to this category for consistency.

Bacterial nanocellulose is a specific category of nanocellulose identified by their specific source of production which is via bacterial fermentation pathways [204]. The diameter of BNC is reported to be within 20–100 nm [205]. BNC is significantly different from other categories based on its nanofiber network with higher crystallinity compared to the others [206,207]. BNC has been reported to be utilized in different field like packaging, biomedical field and energy storage [208–210]. However, to the best of our knowledge, up to now there has been no report of separation performance of BNC in gas separation other than one study reporting CO_2 permeability of this category as the main polymer matrix or additive [211].

3.2. Chitosan

Chitosan (CS) is a derivative of poly(β-(1–4)-N-acetyl-D-glucosamine, the second most abundant bio-based polymer known as chitin, a naturally sourced polysaccharide which can be found in shellfish waste and shells of crustaceans [212]. Characteristics such as low-cost (it is well established as one of the main byproducts of marine processing), non-toxicity, biocompatibility, biodegradability, presence of multiple functional groups, and ease of processibility have made chitin and its derivatives an interesting bio-based polymer for many applications, including gas separation [212,213].

Chitosan (Fig. 3b) is obtained through the deacetylation reaction of chitin, where some acetyl groups ($-COCH_3$) are replaced by amine groups ($-NH_2$), and its properties strongly depends on its deacetylation degree (DD%). Both molecular weight and deacetylation degree of chitosan are controlled via processing condition [212]. Furthermore, like any other naturally based biopolymers, chitin samples contain different amounts of N-acetyl group depending on their origin and isolation procedure which will affect the structure of chitosan as well [214].

The existence of both amino and hydroxyl groups in the structure of this biopolymer has made it an interesting choice of biopolymer for separation applications. Beyond membrane applications, chitosan has also been explored as a CO_2 adsorbent due to its inherent amine groups. Foong et al. reviewed different studies on integration of chitosan with other materials to develop effective CO_2 adsorbents, highlighting key factors influencing enhanced adsorption performance, including synthesis operating conditions [215]. Due to its small specific area and low porosity, chitosan alone is considered unsuitable as a CO_2 adsorbent. Consequently, various studies have attempted to combine this biopolymer with other materials, such as multi-walled carbon nanotubes [216], graphene oxide [217,218], MOFs [219], and Zeolites [220], to leverage chitosan's biodegradability and inherent amine contents.

The hydroxyl group of chitosan gives it a hydrophilic nature resulting in unique properties such as swelling and solvent stability as a basis for membrane production. Although this biopolymer is insoluble in water, the basic nature provided by its amino groups allows it to dissolve in dilute aqueous acetic acid. [69]. Yet, structural modification of chitosan is more challenging than cellulose as chitosan has stronger intermolecular forces [214]. Therefore, chitosan shows lower affinity towards most organic solvents which are crucial for chemical modification reactions which makes it a difficult task to do compared to cellulose.

3.3. Polylactic acid

Polylactic acid (Fig. 3c) derived from lactic acid (2-hydroxy propionic acid) is a linear aliphatic thermoplastic polyester synthesized entirely from renewable agricultural resources. The building block of this biopolymer is known as lactic acid (2-hydroxy propionic acid) existing in two optically active configurations known as the L(+) and D (−) isomers. The ratio of these two isomers defines the material properties such as crystallization tendency. In general, higher crystallinity is promoted by a greater portion of L isomers, giving the material a greater stereochemical purity [182,221–223]. Production involves bacterial fermentation of simple sugars like dextrose obtained from plant-based carbohydrate sources such as corn, rice starches and sugar feedstocks [21,221]. Among the various rigid bioplastics, PLA is one of the most commercially used bio-based polymers due to its compostable nature [224]. Moreover, this polymer is also considered as a promising alternative to petrochemical-derived products since it presents good processibility, mechanical strength and transparency in addition to its environmentally benign characteristics such as its bio-based, biodegradable, and biocompatible nature [18,24,224].

3.4. Other bio-based polymers

Many others bio-based polymers can be considered and have been considered to enhance the separations properties of membranes for carbon capture and are worthy of mention even if they were not used as membrane but more as filler or additives. In the following section, a brief presentation will be given of those materials, which were used, in conjunction with nanocellulose and chitosan, or as substrates for ionic liquids.

3.4.1. Lignin

Lignin (Fig. 3f) constitutes 10–30 % of the mass in lignocellulosic feedstock, depending on the type of the source, acting as a reinforcement for the cell wall [225,226]. Naturally, lignin is produced from polymerization of units, called monolignols, which are cinnamyl alcohols in the cell wall of the plants as a protector against physical damage and water. These monolignols are transferred into 3 types of units found as structural units of lignin: hydroxyphenyl, guaiacyl and syringyl phenylpropane [227,228]. Functional groups like phenolic and aliphatic hydroxyl groups contribute to its potential for chemical modification and moisture sensitivity. Depending on the source of the lignin and pretreatment method used, the proportions of three building blocks may vary, resulting in variations in properties of this biopolymer, like enhancing its hydrophilicity or facilitating the chemical modifications on this biopolymer [228–230].

Despite the presence of hydroxyl groups in the structure of lignin, this biopolymer is less responsive to humidity. This behavior can be explained by the presence of phenolic groups on its main chain. In case of exposure to humidity, lignin structure is affected through elimination of hydrogen bonds among lignin molecules and formation of new H-bonds between water and hydroxyl groups on lignin [227]. The sensitivity to humidity for different types of lignin can vary since the phenolic hydroxyl groups change depending on the pretreatment methods used for each type [231].

3.4.2. Starch

Starch (Fig. 3d) is a renewable and biodegradable polysaccharide, containing about 30 % amylose, 70 % amylopectin and less than 1 % lipids and proteins from plants. Starch is predominantly extracted from agricultural sources such as corn, potatoes, rice, and wheat. Its widespread availability and low cost contribute to its appeal in sustainable material development. As a main component, amylose is composed of a linear chain and constituted the amorphous part of starch granule. In contrast, amylopectin represented branched molecules and contributed to the crystalline component [185]. While pure starch membranes offer environmental benefits, they often exhibit limitations in mechanical strength and gas permeability. To address these issues, modifications such as blending with other polymers, i.e. grafting starch with poly (vinyl alcohol) (PVA) and methacrylate, or chemical cross-linking are employed resulting in greater transport properties, tensile strength and modulus [22,232].

Moreover, the hydroxyl groups (-OH) of starch, that surround the aromatic ring of the polymer chain (Fig. 3d), enhances its affinity for polar gases (such CO_2), thus improving solubility and selectivity [233,234].

3.4.3. Silk fibroin

Derived from silkworm cocoons, silk fibroin is a natural fibrous protein known for its distinctive mechanical robustness, sufficient supply, ease of processing and biocompatibility [76,235]. Silk fiber formation occurs under mild conditions, such as room temperature and in an aqueous environment, making it a compelling material for developing nanomaterials with significant potential [236]. From structural point of view, silk fibroin is a block co-polymer rich in hydrophobic β-sheets linked by small hydrophilic linker segments or spacers, resulting in both crystalline and amorphous regions in the structure [76,237]. The amino acid composition of this material mainly consists of glycine, alanine and sericin accounting for 43 %, 30 % and 12 % of its composition respectively. As illustrated in Fig. 3e, the repeating amino acid sequence in silk fibroin polypeptide chains promotes the formation of a well-organized crystalline structure composed of β-sheets. The β-sheets, also known as high molecular weight chain of SF, are connected to this structural feature which is also the primary driver of the material's self-assembly behavior, while the proportion of crystalline and amorphous regions in the extracted silk fibroin dictates its final property including brittleness from the β-sheet structure [236,237].

On the other hand, the inherent amine groups present in the structure of silk fibroins can serve as a bio-based carrier for CO_2 separation in polymeric membranes, regulatable by temperature and humid conditions [76,238].

4. Bio-based membranes for CO_2 separation

As discussed in previous sections, numerous studies have aimed to characterize bio-based polymeric membranes for this application. A summary of the studies involving the bio-based polymers discussed in this review is provided in Table 1. Most research has focused on characterizing chitosan and nanocellulose, often combined with various fillers, including bio-based ones. This section provides a summary of the properties investigated in each study, such as the effects of temperature, pressure, humidity, and filler/additive load. Some options may not be completely biobased and biodegradable, but they have been mentioned as reference and comparison, to offer a more complete and valuable insight into the properties of biopolymers and to present broader understanding of their potential in the field of carbon capture.

4.1. Cellulose-based membrane for carbon capture applications

Cellulose acetate (CA) is one of the first cellulose-based membranes established as a promising choice for CO_2 separation from CH_4, also at industrial scale [90]. As mentioned before, the degree of substitution plays a determining role in characteristics of cellulose acetate, including its gas separation performance. A study by Puleo et al. shows that higher CO_2 permeability can be achieved with a higher degree of acetylation due to the presence of higher free volume in the structure [39]. At operating conditions of 1 atm and 35 °C, an increase in the degree of substitution from 1.75 to 2.85 led to a rise in CO_2 permeability from 1.84 to 6.56 Barrer. However, this enhancement was accompanied by a slight decrease in CO_2/CH_4 selectivity, from 35.6 to 32.8 respectively. Different strategies have been put into work to improve the separation performance of this material, including incorporating MOFs [41,48], carbon nanotubes [43,48], and thiazole-based polyimines [47].

This material has been reported for separation of CO_2 from N_2 as well. In this case, CO_2 separation is maintained by implementing additives into cellulose acetate polymer matrix in order to achieve a reasonable selectivity regarding the mentioned gas pair. Several additives have been evaluated for using cellulose acetate-based membranes for this application, such as multi-walled carbon nanotubes [43,44], silica [45], Pebax [46], ion-exchanged zeolites [42], MOFs [41], and thiazole-based polyimines [47]. High CO_2 permeability (3000 Barrer at 3 bar and 35 °C) was achieved by incorporating 3 wt% thiazole-based polyimines (PMs), resulting in a CO_2/N_2 permeability-selectivity slightly above the 2019 upper bound, while the CO_2/CH_4 permeability-selectivity remained just below the line set by both the upper bounds [47]. Although cellulose acetate has a long history of commercial application, the performance reported in the above-mentioned studies generally falls below the upper bounds, highlighting the need for continued efforts to optimize cellulose-based membranes.

Ethyl cellulose (EC) is another cellulose derivative that has been investigated for gas separation applications. Although it exhibits relatively high CO_2 permeability compared to other cellulose derivatives (113 Barrer at 25 °C and 2 bar), its overall performance remains below the upper bounds for various gas mixtures [49]. Attempts to enhance EC's properties by incorporating nanofillers to form mixed matrix membranes with ZIF-8-modified GO plates, have not successfully elevated its status despite improvements in CO_2 permeability and CO_2/N_2 selectivity (up to 200 Barrer and 33 respectively) as reported in Table 1 [50].

Distinctive features of cellulose-based derivatives have long been of interest for packaging due to their barrier properties. Further studies on this application revealed that the material's hydrophilicity presents a limitation for its intended use [203,239]. Based on a study by Minelli et al. on mass transport properties of CNF films [240], humidity can result in an adverse decrease of barrier properties through increasing oxygen permeability about two orders of magnitude. However, this challenge can be turned into an advantage by exploiting its hydrophilic nature to enhance the gas separation properties of the biopolymer.

As visible from the data reported in table one, the potential of CNF-based membrane is investigated by means of permeation tests for CO_2, N_2 and CH_4 under various relative humidity in a few studies [51,52]. The swelling caused by water sorption in the polymer matrix enables size-selective gas transport, which gets more pronounced as the water-induced swelling increases. As reported by Ansaloni et al. [51], the highest CO_2 permeability achieved by this study for pure CNF sample is approximately 25 Barrer at 90 % relative humidity, representing a two-order-of-magnitude increase compared to its permeability at 50 % relative humidity, as reported in Fig. 4, while CO_2/N_2 selectivity remained constant and extremely high (in the order of 500). The severe water-induced plasticization, therefore, drastically reduces the superior barrier performance observed in anhydrous environments due to the high gas diffusivity in water. However, the substantial matrix swelling and rearrangement under humid conditions does not decrease membrane selectivity allowing to reach performance well above the 2019 Robeson upper bound. No data are, however, available for thin film membranes which are indeed usually considered in industrial separations.

The same material was tested by Venturi et al. resulting in different separation performance due to a difference in the casting procedure. Skipping a vacuum stage prior to casting in this study resulted in an increase of permeability followed by decrease in selectivity as the size sieving effect becomes less pronounced in a less compact polymer matrix for larger molecules such as N_2 [52]. To enhance separation performance, the transport mechanism can be shifted to facilitated CO_2

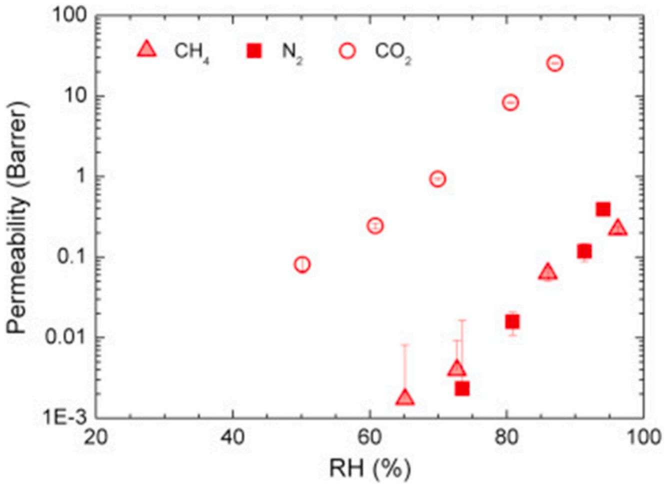

Fig. 4. Permeability of CO_2, CH_4 and N_2 in nanocellulose membranes at different relative humidity at 35 °C and 1 bar [51]. Reprinted with permission.

transport by incorporating amine carriers into the membrane matrix. This approach relies on a reversible chemical reaction between CO_2 and the amine-based carrier sites. In these conditions, the presence of water is essential as facilitates the CO_2 transport process in fixed-site carrier systems by promoting the formation of carbonate and/or carbamate ions and enhancing the regeneration of free amine carriers. This accelerates the "hopping" mechanism of CO_2 between carrier sites [241]. The process is illustrated by the following reactions:

$$CO_2 + R - NH_2 + H_2O \leftrightharpoons HCO_3^- + R - NH_3^+ \tag{5}$$

$$R - NH_2^+COO^- + R - NH_2 \leftrightharpoons R - NH - COO^- + H_3O^+ \tag{6}$$

$$R - NH_2 - COO^- + H_2O \leftrightharpoons R - NH_2 + HCO_3^- \tag{7}$$

The addition of polyvinyl amine (PVAm) to a nanocellulose matrix, therefore, can induce a facilitated transport mechanism of CO_2 (as depicted in Eqs. (5)–(7)), resulting in a significant improvement in CO_2 permeability thanks to facilitated transport mechanisms. Increase of up to 5 times has been reported which however was accompanied by reduction of the selectivity [51,52]. This result has been justified via the excessive swelling of the membrane due to water sorption as PVAm is indeed strongly increasing the hydrophilicity of the developed samples and increase the free volume of the nanocellulose membrane.

Carboxymethylated CNF (cm-CNF) has properties such as surface with a high charge, presence of numerous acidic groups, which can increase the probability of interaction between this biopolymer with other molecules including amino acids often used as CO_2 carrier [53]. Membranes based on cm-CNF with addition of L-arginine were studied for CO_2 separation from N_2 under different relative humidity. The results point to the primary role of L-arginine in improving CO_2 separation performance compared to the effect of water sorption, leading to a seven-fold increase of CO_2 permeability (220 Barrer at 94 % RH) and CO_2/N_2 selectivity of maximum 187 with 45 wt% loading of L-arginine [53]. However, increasing the concentration of amino acid mobile carrier causes a loss of mechanical stability in the film, raising serious concern about the long-term stability and durability required for industrial applications [53]. None of the membranes considered was indeed tested as thin film and still result far from industrial applications.

A recent study evaluated an innovative polymeric combination, termed "artificial wood," incorporating nanocellulose derived from tunicates, combined with lignin and starch [57]. The main polymer matrix in this study is composed of CNF combined with starch, aimed at achieving a densely packed polymer chain structure. The study explored the effects of different types of lignin to better understand the interactions between CNF and lignin in these composite membranes. Notably, the composite membrane containing 5 wt% softwood lignin exhibited extremely high CO_2 permeability, around 1300 Barrer. Based on the permeability results, this membrane demonstrated selectivity for H_2 with respect to CO_2 of 3.7, but surprisingly it appeared ineffective for separating CO_2 from N_2 ($\alpha_{CO2/N2} < 1$).

Janakiram et al. [56] developed nanocellulose–ionic liquid (IL) hybrid membranes that exhibit humidity-responsive CO_2/N_2 separation performance, highlighting a unique molecular gate-opening mechanism triggered by water molecules. The incorporation of 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]) into CNF matrix significantly enhanced the membrane's affinity for CO_2, leading to exceptionally high selectivity values. At 50 wt % [EMIM][Ac] and 90 %RH, the membrane achieved the maximum in CO_2 permeability of 330 Barrer and a selectivity of about 60, which however was not the maximum values observed. At 35 wt % [EMIM][Ac] and 60 % RH, due to humidity-responsive gate-opening mechanism within the 50–70 % relative humidity range, the membranes achieved a $\alpha_{CO2/N2}$ of 370 coupled with a CO_2 permeability in the order of 40 Barrer as demonstrated by mixed-gas permeation tests conducted at 35 °C, 1.7 bar.

Nanocellulose in its various forms has been often used to increase membrane stability and performance due to mechanical properties, abundance of charge on its surface and hydrophilicity, acting in favor of CO_2 separation ability, as reported in Table 1 where nanocellulose-based membrane reported great selectivity of CO_2 versus other gases. Many studies have been carried out to investigate the effect of cellulose nanocrystals as a filler for membranes based on polyvinyl alcohol (PVA) for both carbon capture application and biogas purification [62–64]. The results indicate a higher permeability of CO_2 upon introducing CNC as a filler. This conclusion is further supported by another study conducted by Janakiram et al. [60], which included an evaluation of the impact of incorporating CNF versus carboxymethylated nanocellulose (cm-CNF) as a filler in PVA-based membranes. Addition of 10 wt % cm-CNF in a PVA-based membrane resulted in a 43 % increase in CO_2 permeance reaching a value of 345 GPU with an increase in CO_2/N_2 selectivity from 30 to 40 at T = 35 °C and P = 1.7 bar. Such effect was not observed in case of adding CNF as a filler to the thin-composite PVA matrix, in which a slight decrease of 8 % in CO_2 permeance was observed. This effect is attributed to the presence of ionic salt and deprotonated -COO⁻ in carboxymethylated nanocellulose causing higher affinity for CO_2 molecules. A significant improvement was observed by functionalizing CNF using amine-containing moieties like PPG, PEG and β-alanine. Among them, β-alanine was chosen as a CO_2-philic amino acid to act as the bio-based amine carrier and managed to further increase CO_2 solubility, resulting in a moderate enhancement of CO_2 permeance up to 263 GPU and CO_2/N_2 selectivity to 50 compared to neat PVA (240 GPU).

The results also indicate that changing the matrix highlighted the effect of these nanofillers on separation performance of the studied membranes. A flat-sheet thin film supported membrane composed by sterically hindered polyallylamine (SHPAA) and PVA, reached permeance of 227 GPU at T = 35 °C and P = 1.7 bar, but they further improved it with the addition of polyethylene glycol (PEG) which created sites for water cluster retention, enhancing CO_2 solubility. This modification led to a significant increase of CO_2 permeance of up to 652 GPU coupled with a CO_2/N_2 selectivity of 41.3 [60]. These results, albeit of interest, are still below the commercial membranes usually considered for post combustion carbon capture applications. For example, Polaris® Gen 1, produced by MTR, is endowed with CO_2 permeance of 1000 GPU and CO_2/N_2 selectivity in the order of 50 [119,242].

The study conducted by Helberg et al. [64] emphasized on the role of the charge and size of CNF in PVA membrane. Phosphorylated CNF was used as an additive in this study to utilize the high charge of phosphoryl groups thanks to an additional milling step, which promoted the intrusion of chemicals for higher final charge. The chemically modified fibers were also further processed via ultracentrifuge for size screening of the fibers in order to select only finer fibers for the membrane preparation. The modifications described in this study led to a 160 % increase in CO_2 permeability compared to neat PVA, for both the batch with increased surface charge and the batch subjected to an additional size-screening step, reaching values of 100 and 116 Barrer, respectively.

Further studies on incorporating nanocellulose (in both forms of CNC and CNF) into a PVA polymer matrix have demonstrated the stability of these systems for industrial applications [61]. The fabricated hollow fiber membranes maintained stable performance for 40 h of continuous operation without any decline. Additionally, tests conducted after storing the material for one year confirmed its long-term stability.

As indicated in Table 1, other studies have also emphasized the role of the charge made available by nanocellulose to PVA membrane [63]. A TEMPO-oxidized CNF was employed to introduce varying surface charges on the fibrils, enabling the investigation of charge effects on gas separation performance. This was compared with phosphorylated CNF, which carries a higher surface charge. Among the tested materials, the PVA/CNC nanocomposite exhibited the most promising performance, achieving a CO_2 permeance of 127.8 GPU and a CO_2/N_2 separation factor of 36—making it a competitive bio-based alternative to carbon nanotube-based membranes. In this system, CO_2 transport is facilitated through specific diffusion pathways influenced by the nanocellulose's surface charge and dispersibility. These pathways are further affected by the hydrophilicity and charge of the nanocellulose, which lead to the formation of non-uniform water-rich regions concentrated around the nanocellulose surface (as illustrated in Fig. 5). A higher surface charge on nanocellulose promotes greater water accumulation and, due to CO_2's polar nature, enhances its dissolution, resulting in the highest CO_2 permeance observed with CNC.

The addition of CNC to the PVA matrix was also investigated for CO_2/CH_4 separation [62]. In addition to exploring the influence of CNC concentration, the effect of pH variation was also studied. Higher CNC content positively impacted CO_2 transport by improving the swelling behavior, which facilitated CO_2 transport through high solubility of CO_2 in water and by increasing the free volume within the system. Increasing the pH by adding NaOH further enhanced CO_2 transport through a reversible reaction, as described in Eq. (9) and Eq. (10). Moreover, the higher pH promoted greater swelling, which contributed to higher CO_2 transport via solution diffusion. The system was evaluated for CO_2/CH_4 separation, with the optimal performance achieved by the sample containing 1 wt % CNC at pH 10, resulting in a CO_2 permeance of 107 GPU and a CO_2/CH_4 selectivity of 43 (under 5 bar pressure and 93 % RH).

$$CO_2 + H_2O \leftrightharpoons H_2CO_3 \tag{8}$$

$$H_2CO_3 + NaOH \leftrightharpoons NaHCO_3 + H_2O \tag{9}$$

$$NaHCO_3 \leftrightharpoons NaOH + CO_2 \tag{10}$$

Dai et al. [67] has reported that only 5 wt % CNC addition to Pebax structure causes 42 % and 18 % increase of humid CO_2 permeability (305.7 Barrer) and CO_2/N_2 selectivity (41.6), respectively, compared to neat material. A recent study investigated a mixed matrix membrane (MMM) composed of polyethylene oxide (PEO), specifically poly (ether-block-amide) (PEBA), and polyurethane (PU), incorporating cellulose nanocrystals as a filler to enhance mechanical and thermal stability. The findings revealed that, even without functionalization to improve interfacial adhesion between CNCs and the polymer matrix, the membrane maintained a satisfactory level of structural integrity [68]. Transport properties were also positively affected by the addition of nanocrystals with optimal results obtained at 1 wt % loading. In this condition, PEBA MMMs showed a CO_2 permeability of 22 Barrer with an ideal CO_2/N_2 selectivity of 73.6 corresponding to an increase of 30 % for both quantities with respect to the neat polymer values.

The effect of different derivatives of CNC, such as phosphorylated and carboxymethylated CNC, as fillers in PVA/L-arginine-based membranes have been also evaluated for biogas purification application [65, 66]. In this study, a hollow fiber membrane configuration was used, where a highly porous poly(ether-sulfone) (PESF) substrate was coated with the selective layer. Gas permeation tests conducted at 1 bar and 90 % of relative humidity revealed that incorporating phosphorylated CNC resulted in higher CO_2 permeability (21177 Barrer) and CO_2/CH_4 selectivity of 33. Moreover, the CO_2 permeance was significantly higher when phosphorylated CNC was used compared to carboxymethylated CNC (13072 GPU vs. 6226 GPU); this fact was attributed to both improved CO_2 transport properties and the formation of thinner selective layers. The overall results are indeed of high interest and surpass those usually considered suitable for highly efficient carbon capture membranes [119,242–245].

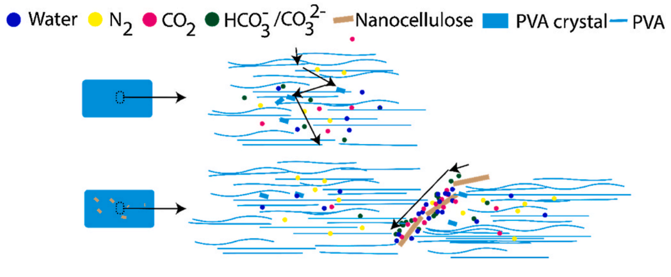

Fig. 5. Redistribution of water in PVA matrix due to charge available by nanocellulose [63]. Reprinted with permission.

Research on nanocellulose-based membranes for CO_2 separation has also focused on enhancing separation performance by incorporating other non-biobased carriers to selectively improve CO_2 transport like MOFs. Dispersing amine-functionalized Zirconium-based MOF (UiO-66-NH_2) in carboxymethylated CNF polymer matrix created acid-based interactions and electrostatic force resulting in an ideal interfacial morphology. The passage of CO_2 in this system is favored by amine groups acting as carriers as well as by the precise expansion in CNF structure by introduction of UiO-66-NH_2. The gas permeation tests conducted at 25 °C demonstrate CO_2 permeability of 139 Barrer and CO_2/N_2 selectivity of 46 under dry condition [59]. A similar study achieved promising results under dry conditions by in-situ growth of a zinc-based MOF (ZIF-8) on TEMPO-oxidized CNF. Single-gas permeation tests at 25 °C and 1 bar of feed pressure showed separation performance exceeding 2008 Robeson upper bound, with a CO_2 permeability of 550 Barrer and separation factors of 45.5 and 36.2 for CO_2/N_2 and CO_2/CH_4 respectively [58].

4.2. *Chitosan-based membrane for carbon capture applications*

In open literature, several studies can be found, evaluating the separation performance of chitosan-based membranes either used as pure, or in composite or even as a filler in other structures; the corresponding results have been already summarized in Table 1 and will be discussed more in detail in this section.

Early studies of chitosan for gas separation applications were carried out in 1997 with the recognition that humidity can result in a significantly improved CO_2 permeability with respect to the poorly permeable dry chitosan. However, the presence of water vapor may accelerate degradation due to swelling of the polymer matrix, which reduces its mechanical stability [246,247]. In addition, some thermogravimetric studies have shown that elevated temperatures also have a detrimental effect on chitosan membranes by identifying thermal decomposition above 200 °C [248,249]. Despite the use of synthetic support for casting the membrane (Polypropylene), this study reported an increase of CO_2 permeability under humid conditions - from 3 to almost 10 Barrer – as relative humidity increases from 80 % to 100 %. This CO_2 permeability, however, corresponded to a decrease in CO_2/N_2 selectivity from 73 to 54 due to the membrane swelling in humid conditions [69].

In the same period, Bae et al. [250] evaluated the CO_2 permeability of pure chitosan membranes in both dry and humid state by casting a self-standing film with a thickness of 50 μm under constant pressure. They stated that the permeability of CO_2 and N_2 in pure chitosan membrane in presence of vapor-saturated gas feed increased more than 15 times compared to dry condition values. Lower increase was instead observed for CO_2/N_2 selectivity which never exceeded the value of 40. Thereby, the presence of water vapor increases the driving force for CO_2 transport, still maintaining the membrane thermal and chemical stability even at high humidity.

Prior research clearly highlights the important role of water in the transport of CO_2 across chitosan-based membranes. This effect is largely attributed to the presence of amine groups in the chitosan backbone, which enables facilitated transport for CO_2 in the membranes (as reported in Eq. (5)). This mechanism is strongly favored by the presence of water through the reactions presented by Eq. (6) and Eq. (7). Unlike many other polymeric systems that require the addition of aminated carriers, chitosan can inherently support facilitated CO_2 transport due to its intrinsic amine functionalities and the presence of water favors the complex-formation reaction between carbon dioxide and amines as it could help in catalyzing carbamic acid reactions.

This effect was indeed investigated in the open literature, as recalled in Table 1, where several studies are found analyzing how water alters the CO_2 gas transport mechanism in chitosan membrane [65,72–75,78, 244,245]. The presence of water results in the swelling of chitosan and induces a facilitated transport of CO_2 through the membrane thanks to the amine groups, which act like fixed site carriers activated by water [70,251]. Based on the study of El-Azzami & Grulke [252], two states of water are present in swollen chitosan: free and bound through hydrogen bonding. Bound water has a significant contribution to the increase of free volume upon sorption and, as a result, to the increase in permeation. This statement can be further verified based on the experimental results performed by the same group using a feed gas mixture of CO_2, N_2 and H_2 over temperature and pressure range of 20–150 °C and 1.5–5 atm. The permeability of CO_2 reaches a maximum of 482 Barrer at temperature of 110 °C and pressure of 1.5 atm where all free water has evaporated, and the effect of bound water can be observed. The maximum CO_2/N_2 and CO_2/H_2 selectivity (250 and 43.4 respectively) is at the same point of reaching maximum permeability considering the feed relative humidity [70]. Above this temperature, the loss of free water in the swollen membrane drastically reduces the facilitated transport pathway, causing a decline in stability and mechanical integrity resistance [70].

Although the permeability-selectivity of the mentioned membrane by El-Azzami & Grulke [70] is significantly high and beyond the 2008 Robeson upper bound, they were able to further enhance the separation efficiency through the addition of Sodium Arginine as a filler [71]. Arginine salts, indeed, act as an additional mobile carrier in the membrane, which increases both transport efficiency and water uptake of the membrane. Permeation experiments conducted over a temperature range of 20 °C–150 °C at around 40 % of relative humidity revealed a maximum CO_2 permeability of 1500 Barrer obtained at 1.5 bar and 110 °C. This modification also resulted in high selectivity values, with CO_2/N_2 and CO_2/H_2 selectivity reaching 852 and 144 respectively, hence the better placing with respect to the upper bound.

Similar to Arginine, other naturally found amino acids have been used as amine carriers in chitosan-based membranes, including L-tyrosine and phenylalanine. Katare et al. [79] conducted mixed gas permeation tests at 85 °C and 2.2 bar to evaluate the influence of chemical grafting and blending of phenylalanine on the separation performance of thin-layer membranes for CO_2/N_2 mixture. Amine blending has resulted in a higher CO_2 permeance (106 GPU compared to 72 in case of chemical grafting) while the CO_2/N_2 selectivity on both blending and grafting methods is rather similar (89 and 97 respectively). The robustness of the fabricated membranes was also evaluated through a 400-h long permeation test, which indicated a more stable performance for the blending method since the membrane maintained sufficient durability and mechanical strength for operational use. The same group also investigated the efficiency of an amine-grafted chitosan for membrane-based post combustion carbon capture [78]. L-tyrosine-grafted chitosan was cast on a porous PES support creating a selective layer of 600 nm thickness. The developed membrane was tested at temperatures ranging from 25 °C to 115 °C at 2.2 bar as well as variable

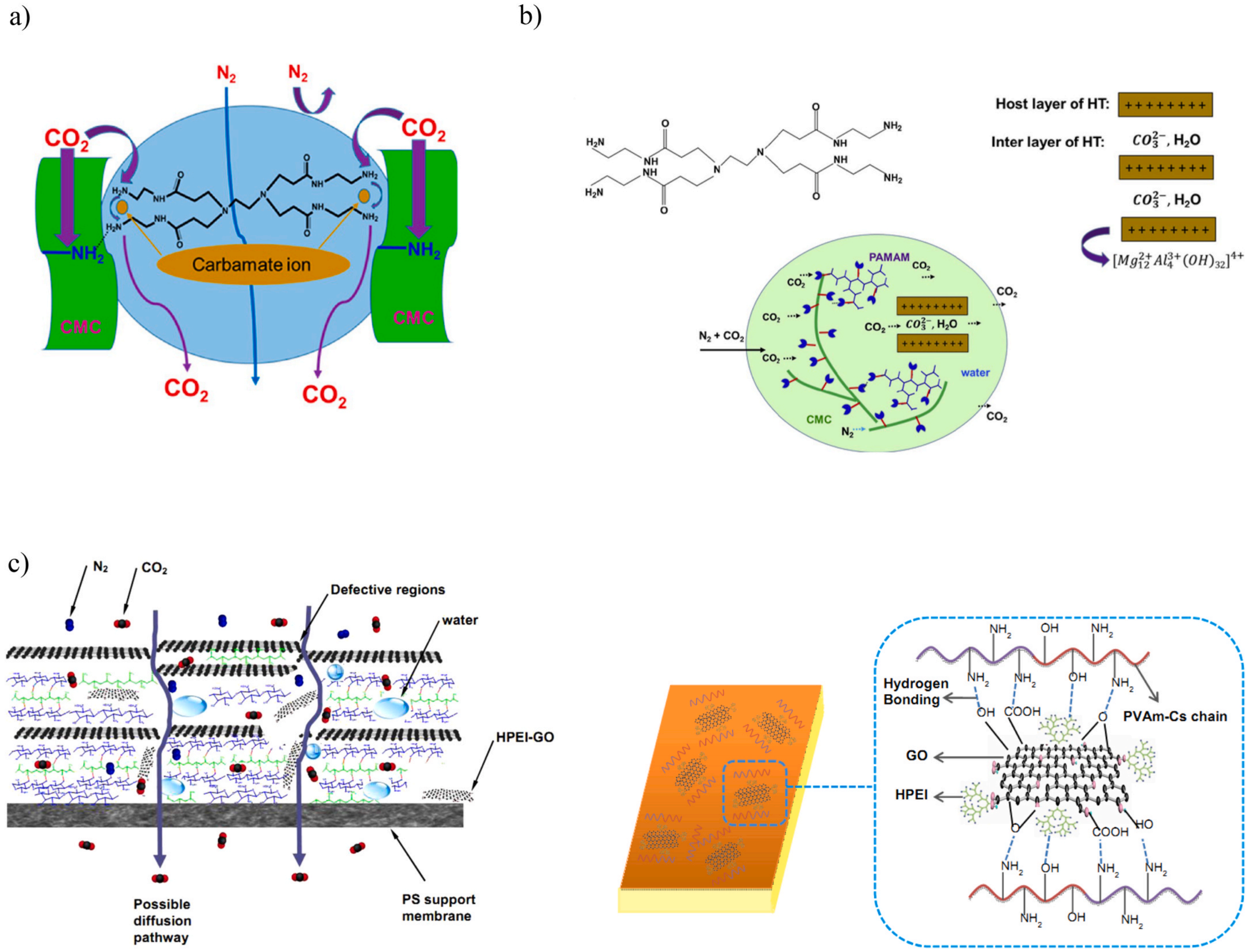

Fig. 6. Scheme and mechanism of gas transport through a) cm-Chitosan/PAMAM [73] b) cm-Chitosan/PAMAM/Hydrotalcite [74], c) PVA/Chitosan/HPEI-GO [80]. Reprinted with permission.

moisture content of the sweep flow. Unfortunately, even the optimal performance of the developed membrane (permeance of 103 GPU and CO_2/N_2 selectivity of 31 at 85 °C and 2.2 bar) was not able to surpass the 2008 Robeson upper bound and remained well below commercially available membranes for post combustion carbon capture [242,243].

Chitosan-based membranes have also been studied in combination with ionic liquids to enhance CO_2 separation. The addition of 5 wt % [EMIM][Ac] to chitosan resulted in high CO_2 permeability, from 1293 to 1338 Barrer at 25 and50 °C, respectively, under a pressure difference of 0.5 bar. However, the CO_2/N_2 selectivity remained relatively low at 4.6 [77].

Shen et al. [80] developed a mixed matrix membrane based on PVAm and chitosan, incorporating GO nanosheets modified with hyperbranched polyethyleneimine (HPEI) as nanofiller (Fig. 6c). Similar to the study by Prasad et al. [76], the graphene derivative serves to enhance membrane durability under humid conditions by intercalating water within its layers. Facilitated CO_2 transport is enabled by the primary amine groups in both PVAm and HPEI. The improved separation performance is primarily attributed to these amine-rich components, while chitosan mainly contributes to higher water uptake, promoting optimal CO_2 transport conditions. Gas permeation tests at 25 °C, 1 bar, and 80 % relative humidity yielded a CO_2 permeance of 112 Barrer and a CO_2/N_2 selectivity of 107 for the PVAm/CS membrane with 3 wt % HPEI-GO.

Shen et al. also employed PEI as the amine carrier in a chitosan-based membrane [75]. To improve miscibility, however, they used carboxymethylated chitosan, taking advantage of its amine and carboxylic acid functionalities. For mixed gas permeation tests at 30 °C under a 0.2 bar partial pressure difference they reported a CO_2 permeance of 630 GPU and a CO_2/N_2 selectivity of 325. Membranes however were very sensitive to feed gas pressure, which when increased up to 0.4 bar substantially reduced both permeance and separation factor.

Further studies using carboxymethylated chitosan incorporated other amine carriers such as piperazine (PZ) [72] and polyamidoamine (PAMAM) [73,74]. In such studies, Borgohain et al. evaluated the effect of PZ loading and reported CO_2 permeances of 72 GPU and 47 GPU, with selectivity of 102 and 55 for 20 wt % and 40 wt % PZ, respectively. The reduced separation performance at higher loadings was attributed to agglomeration of PZ, which hindered CO_2 transport by disrupting the membrane structure.

The same research group also investigated PAMAM as amine carrier, revealing additional mechanisms beyond conventional facilitated transport (Fig. 6 a and b). They discovered a pH-responsive molecular gate effect, where the formation of carbamates between CO_2 and amines leads to dendrimer crosslinking, inhibiting N_2 permeation [73]. Additionally, chitosan's polyelectrolyte nature induces a salting-out effect, further suppressing N_2 solubility and enhancing CO_2 selectivity. Gas permeation tests from 60 °C to 110 °C at 2 bars showed optimal CO_2 permeance of 98 GPU and a CO_2/N_2 selectivity of 149 for samples containing 10 wt % of PAMAM. It has been observed that the higher content of this amine carrier deteriorates the gas separation due to self-aggregation of PAMAM at higher percentages, leading to suppression of amine active sites. Subsequent modification of the system with hydrotalcite (HT) as inorganic filler introduced hydrated carbonate anions into the membrane [74]. The hydrated carbonate anions facilitate CO_2 transport by surfing through HT interlayers based on the reaction described in Eq. (11).

$$CO_2 + CO_3^{2-} + H_2O \leftrightharpoons 2HCO_3^- \tag{11}$$

This modification slightly improved CO_2 permeance (to 123 GPU), but also led to a decline in selectivity, reducing the CO_2/N_2 separation factor to 67.

As mentioned in Section 3.4, silk fibroin (SF) is another bio-based material with inherent amine groups that can serve as a carrier in the development of fully bio-based membrane systems. Prasad et al. [76, 238] developed a MMM using chitosan as the polymer matrix, silk fibroin contributes to the CO_2 facilitated transport and graphene nanoparticles (GNP) to mitigate support pore blockage and enhance the long-term stability of membrane separation performance. In this system, the incorporation of SF facilitates CO_2 transport via its amine groups, increasing CO_2 permeance from 46 GPU (for chitosan/GNP) to 159 GPU at 90 °C and 2 bar feed pressure. Mixed-gas permeation tests using a ternary gas mixture of CO_2, N_2, and H_2 showed a maximum CO_2 permeance of 126 GPU, with a CO_2/N_2 selectivity of 104 and a CO_2/H_2 selectivity of 52, highlighting its potential for fuel cell applications.

4.3. PLA-based membrane for carbon capture applications

Early studies on PLA properties for gas separation were carried out by Lehermeier et al. through evaluating the effect of crystallinity on permeation of gases (N_2, O_2, CO_2 and CH_4) both in pure and mixtures, showing good results for H_2 separation [223]. However, PLA in its pure form exhibits limitations in gas separation applications due to its rigidity and brittleness that reduces the gas permeability and selectivity. Moreover, PLA membranes are susceptible to environmental degradation, including hydrolytic and microbial degradation, especially at elevated temperatures (above 60 °C) and neutral pH (pH 7.4), thus limiting its long-term stability [253]. The properties of these materials are typically inadequate for efficient CO_2 separation, especially when compared to other high-performance polymers commonly used in this field. To overcome these limitations, further research has been carried out on modifying PLA-based membranes to enhance their performance as mentioned in Table 1. Indeed, the solubility of PLA in many non-polar solvents gives this polymer the advantage of simple membrane fabrication via solvent evaporation or phase inversion [254].

Several strategies have been explored, such as blending PLA with other polymers, incorporating fillers like nanocellulose, carbon nanotubes and chemical modifications to improve PLA's properties. The incorporation of those fillers increases the chain mobility and the polymer's fractional free volume, potentially affecting both the durability, mechanical stability and separation performance of the hybrid membranes [255].

Most studies have focused on evaluating PLA as a barrier material for packaging applications, where low gas permeability is essential. As a result, PLA has been reported to exhibit CO_2 permeability values below 1 Barrer, with some studies indicating values several orders of magnitude lower [255–259]. Other studies, however, also focused on the performance of this material for membrane-based gas separation via single-gas permeation tests under dry conditions unlike other biopolymers discussed in this review. The difference in experimental condition can be attributed to the high sensitivity of PLA-based materials to humidity and possibility of degradation as evaluated for packaging applications despite the hydrophobic nature of PLA compared to other biopolymers [260,261]. The permeability and selectivity of different gases have been seen to depend on the membrane fabrication method and on the type of PLA, affecting the final application significantly. It should be mentioned, in this regard, that no post-combustion application for PLA-based membranes were identified and as a result mainly data regarding separation of CO_2 from CH_4 were found in the literature.

A CO_2 permeability of 11 has been reported, by Iulianelli et al., for a PLA-based membrane at ambient temperature, corresponding to a CO_2/CH_4 selectivity between 220 and 230 [83]. The same research group also reported data related to pre-combustion capture, where PLA-based membranes also in this case were able to surpass the upper bound for H_2/CO_2 separation, though with relatively low permeabilities, such as 25 Barrer for H_2 [82]. To emphasize the type of PLA used for developing the membrane, Iulianelli et al. [81] fabricated dense symmetric membranes from a commercial grade PLA using the phase inversion technique. No further information on the modification of PLA was reported in this case. Gas permeability and selectivity performances of the membrane were evaluated for different single gases (H_2, CH_4, CO_2, and He) at room temperature (Table 1). Single-gas permeation tests revealed the significant deviation of CO_2 permeability from the theoretical correlation within permeability and critical volume, confirming the strong influence of solubility on enhanced permeability of CO_2 while the behavior of other gases was mostly controlled by diffusion. The authors reported a CO_2 permeability of up to 70 Barrer at 25 °C under dry condition, surpassing the Robeson upper bound for CO_2/CH_4 separation with a selectivity of 285, indicating promising potential for biogas separation applications (Fig. 7).

This biopolymer was also evaluated for the transport properties of CO_2-rich mixtures, specifically for CO_2/CO separation. Checchetto et al. [84] conducted mixed-gas permeation tests using ternary mixture ($CO_2/CO/O_2$) and reported the CO_2 permeability of 1.1 Barrer at 25 °C. Based on single-gas permeation tests conducted, a CO_2/N_2 selectivity of 22.4 can be achieved (at 25 °C and feed pressure between 20 and 90 kPa).

Among the various applications of PLA, its use in gas–liquid membrane contactors for carbon capture processes are particularly noteworthy. The results of this study highlight the potential of this biopolymer to achieve greener, more sustainable CCU technologies [262].

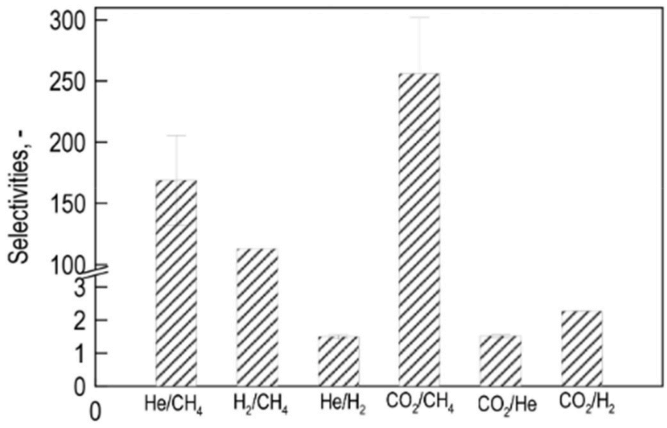

Fig. 7. Selectivity of CO2, He, H2 and CH4 at 25 °C in PLA Easy Fil TM - White membranes from Ref. [81]. Reprinted with permission.

5. Performance of polymeric membranes against upper bounds for carbon capture

As discussed in Section 2.1, the performance of polymeric membranes is commonly assessed by their placement against the upper bounds, which depicts the well-known trade-off between the two mains properties: CO_2 permeability and selectivity. In this review, the bio-based membranes have been plotted against the CO_2/N_2 and CO_2/CH_4 upper bounds, presented in Figs. 8 and 9, respectively. While Section 4 focused on the role of different transport mechanisms and carriers in enhancing the separation performance of bio-based materials, the present section evaluates the overall trends followed by both fossil-derived and bio-based polymeric membranes with respect to the upper bounds.

Apart from the number of studies reported in these two figures, it is clear that research on bio-based membranes for carbon capture has predominantly centered on CO_2/N_2 separation. The outcome is also more promising for this gas pair based on the number of cases surpassing the upper bounds as depicted in Fig. 8.

When CO_2/N_2 performance is plotted against the upper bounds, a different behavior clearly emerges between fossil-derived polymers (Fig. 2a) and bio-based systems (Fig. 8). In conventional petroleum-based membranes, only a limited subset of high free-volume materials (most notably PIMs and their derivative with high FFV) are able to cross the Robeson upper bound thanks to their extremely high permeability which offset their average values of selectivity; the majority of commercial engineering polymers (polyimides, polysulfones, polycarbonates, etc.) remain below the envelope, despite the broad CO_2 permeability which ranges from 10 to 10^5 Barrer. In contrast, bio-based materials generally operate in a lower permeability range (between 10 and 300 Barrer) where these bio-derived polymers are able to surpass the upper bound by enabling facilitated transport which boost their selectivity.

The upper bounds have been surpassed by neat biopolymers by different materials based on both CNF and Chitosan. CNF under humid conditions in particular exhibited exceptionally high selectivity for CO_2/N_2 separation despite low CO_2 permeability, resulting in its position in top left part of the plot presented in Fig. 8, but surpassed the upper bounds also when added with different components such as amino-acids, zeolites and ionic liquids, which presents both permeability and selectivity above 100. However most performing materials are based on chitosan. Membranes where it was coupled with amine carrier as PEI reached extremely high permeability and separation factors in the low pressure range, while when mixed with arginine salt managed to surpass this limit at high temperature (up to 150 °C) as amine groups can accelerate the facilitated transport of CO_2 in these conditions.

These observations indicate that for bio-based systems, performance enhancement is not primarily achieved via high free-volume architectures but rather through specific chemical affinity to CO_2, meaning that the upper bounds can be surpassed through sorption-selectivity mechanisms (facilitated transport) rather than solution-diffusion.

For CO_2/CH_4 separation, on the other hand, only a limited number of bio-based polymers overcome the upper bounds, particularly cases based on CNF and PLA. The properties of these membranes however do not overcome those of synthetic membrane reported in Fig. 2b, where polyimides (e.g. PI, Matrimid), poly(p-phenylene oxide), and different grades of PIMs dominate the upper-right region of the plot.

Very likely most of the facilitated transport membranes tested for CO_2/N_2 will show very interesting performance also in the case of methane separation but they were not tested for that purpose. Therefore, in the lack of actual experimental data, petroleum-derived polymers still represent the most competitive class of materials, primarily due to their intrinsically high CO_2 permeability. This kind of separation on the other hand is already a mature market for membranes and that makes it even more difficult for new materials to find their spot.

In this concern, it should be noted that, despite the promising results, only a few of the biopolymers tested were successfully processed into thin-film configurations, and even fewer demonstrated encouraging performance in terms of mechanical integrity and thermal stability, thereby surpassing the membranes currently used at industrial scale [242–244]. Moreover, to the best of the author’s knowledge, none have yet been evaluated at pilot or semi-pilot scale, making any commercial application still a distant prospect.

6. Conclusions

The escalating need to reduce CO_2 emissions has intensified global efforts toward developing sustainable carbon capture technologies. Among these, membrane-based gas separation presents a promising low-energy alternative to conventional processes and possibly also a green solution when membranes based on sustainable bio-materials are considered. The use of bio-based polymers has indeed attracted growing attention, also in the field of membranes not only for their environmental compatibility, biodegradability, but also for the possibility of tuning their physicochemical properties to obtain high selectivity and permeability in liner to those typical of fossil-based polymers.

This review has explored a wide range of bio-based membrane materials, focusing mainly on cellulose derivatives, nanocellulose, chitosan and polylactic acid (PLA) even if other naturally derived polymers have been also considered. These materials have demonstrated varying degrees of potential for CO_2 separation, based on gas transport properties such as permeability and selectivity being evaluated against the well-known upper bounds, depicting their performance with respect to the

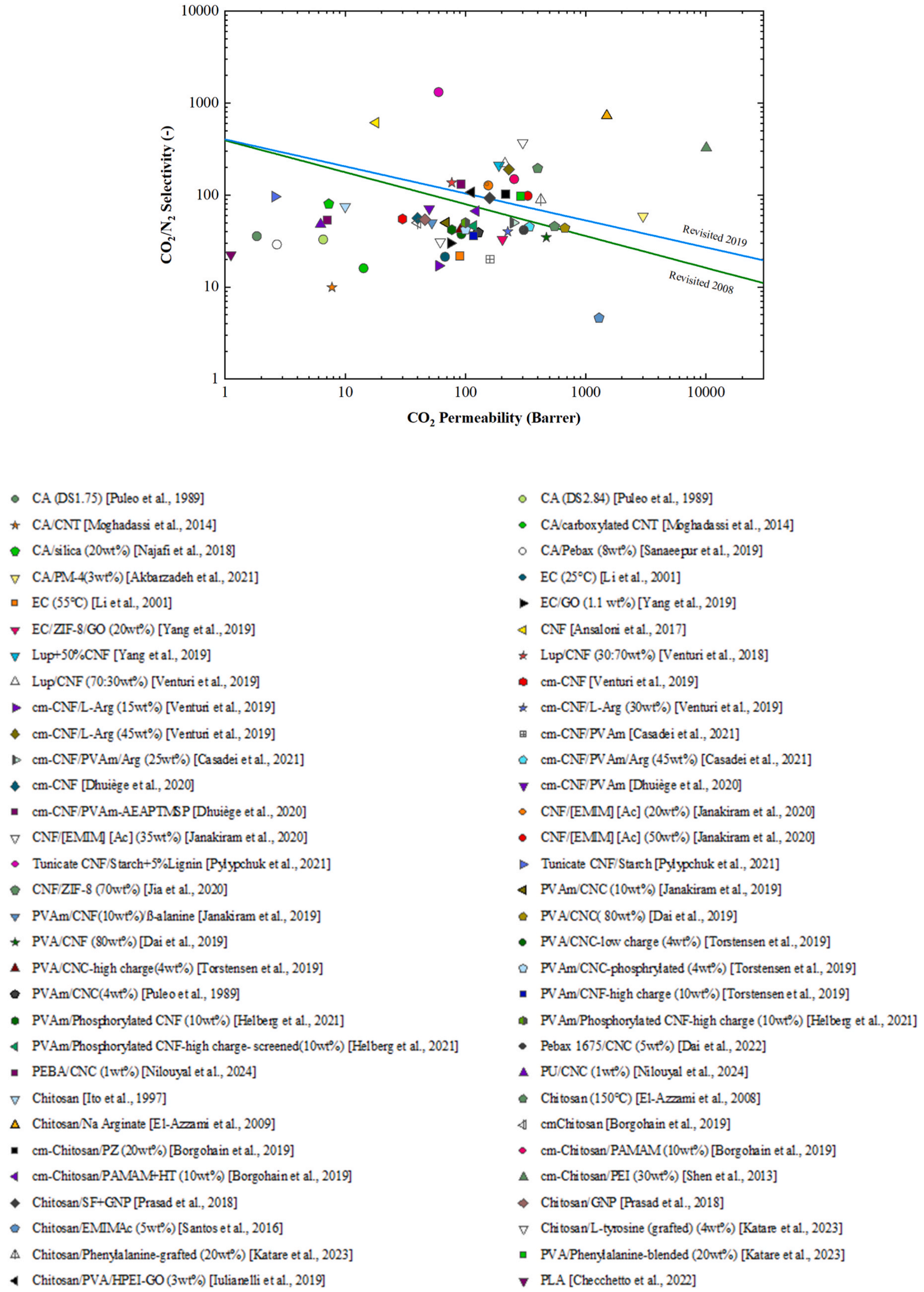

Fig. 8. Bio-based studies against upper bounds for CO_2/N_2.

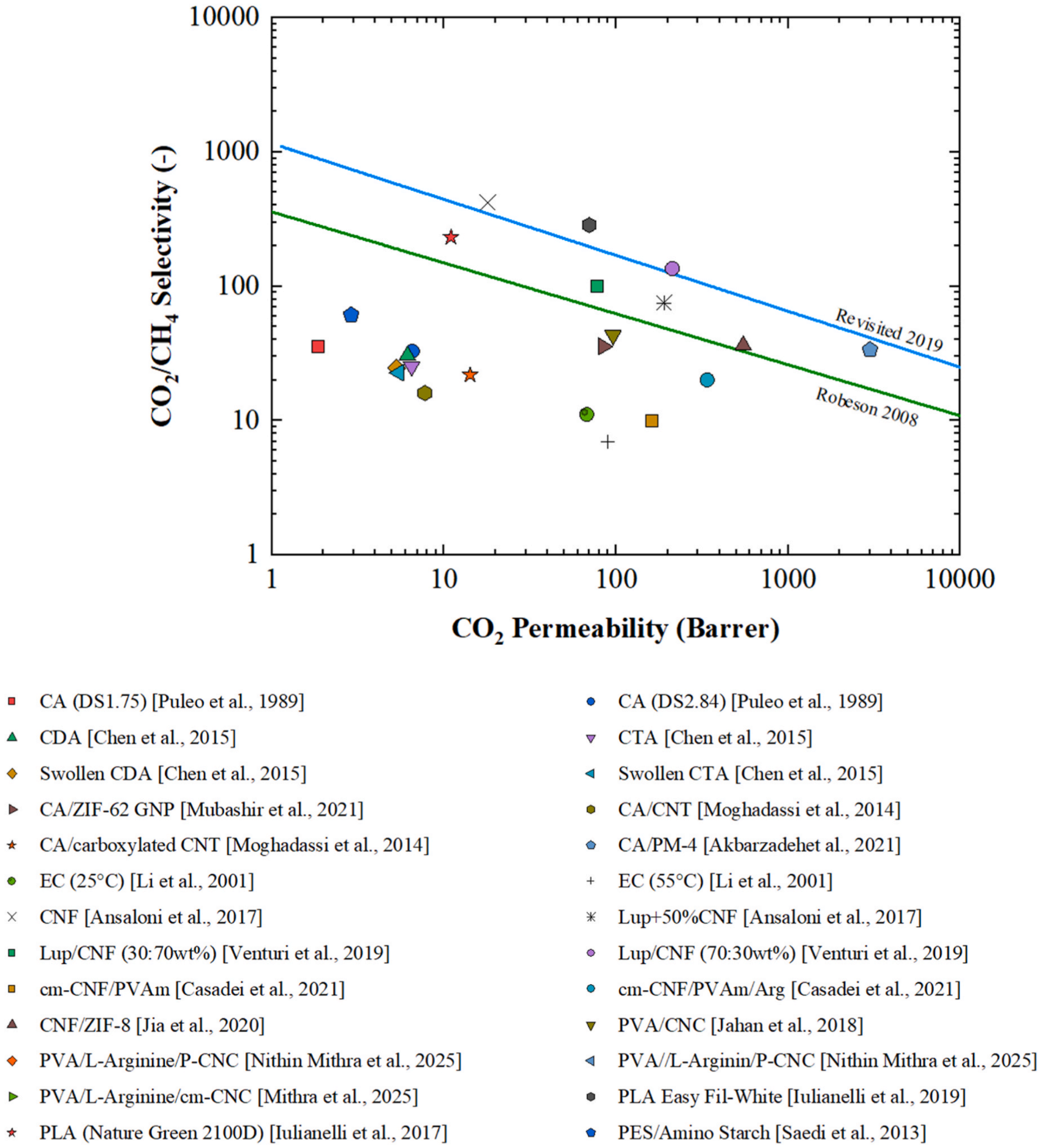

Fig. 9. Bio-based studies against upper bounds for CO_2/CH_4.

trade-off effect. While conventional cellulose acetate is already used industrially, other derivatives such as carboxymethylated or phosphorylated cellulose have shown extremely interesting results. Nanocellulose-based materials have also emerged as one of the most extensively studied and versatile bio-based polymers for membrane development. Owing to their unique combination of renewability, mechanical strength, high surface area, and tunable surface chemistry, both cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) have been successfully integrated into polymeric matrices and mixed matrix membranes for CO_2 separation. Nanocellulose based materials have proven to be able to surpass Robeson's Upper Bound, especially if coupled with selective carriers able to activate facilitated transport inside the membrane.

Chitosan, stands out as well, among the different biomaterials, due to its intrinsic amine functionality, which enables facilitated transport of CO_2 without the need for additional carriers. This characteristic, along with its hydrophilic nature and pH responsiveness, makes Chitosan an ideal platform for developing membranes that operate efficiently under humid or chemically dynamic conditions. Its integration with ionic liquids, polyimines, and advanced fillers like graphene oxide or MOFs has led to remarkable improvements in CO_2 permeability and selectivity. Also, in this case several of these membranes were able to obtain superior performances with respect to the Robeson upper bound.

PLA has been investigated in view of its application as gas separation membrane, even if to a lower extent with respect to previous materials. This is likely due to the lower performance which made this biopolymer less appealing than the Chitosan and Nanocellulose.

In general, several bio-based membranes have approached or even surpassed Robeson's 2008 and 2019 upper bounds for gas pairs like CO_2/CH_4 and CO_2/N_2, suggesting that the long-held permeability–selectivity trade-off may be overcome with optimized biohybrid designs.

Despite these advancements, challenges remain. Issues such as mechanical stability, long-term durability, processability, and compatibility with synthetic additives must be further addressed. Most current studies are still limited to lab-scale evaluations under controlled conditions. For broader adoption, future work must focus on.

- Understanding long-term membrane behavior under real flue gas or biogas compositions
- Optimizing interfacial compatibility between bio-based matrices and functional fillers
- Developing fully bio-based or recyclable composite systems based on industrial application

In this concern, a complete lifecycle assessment should be considered for the most promising materials to understand and quantify the environmental benefit that their use can bring with respect to synthetic polymer in the field of CO_2 removal.

In summary, bio-based polymeric membranes surely represent a viable and environmentally sustainable pathway toward next-generation CO_2 separation technologies, even if a lot of research is still needed to make them a real alternative to other industrially available solutions.

CRediT authorship contribution statement

Zahra Maghazeh: Conceptualization, Data curation, Formal analysis, Writing – original draft. **Virginia Signorini:** Conceptualization, Methodology, Writing – review & editing. **Marco Giacinti Baschetti:** Supervision, Validation, Writing – review & editing.

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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Data availability

Data will be made available on request.

References

[1] R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, Sci. Adv. 3 (2017), https://doi.org/10.1126/SCIADV.1700782/SUPPL_FILE/1700782_SM.PDF.
[2] J. Zheng, S. Suh, Strategies to reduce the global carbon footprint of plastics, Nat. Clim. Change 9 (2019) 374–378, https://doi.org/10.1038/S41558-019-0459-Z.
[3] D. Spiegel-Feld, K.M. Wyman, International environmental actors: the case of marine plastics, Ariz. Law Rev. 62 (2020).
[4] N.S.K. Gowthaman, H.N. Lim, T.R. Sreeraj, A. Amalraj, S. Gopi, Advantages of biopolymers over synthetic polymers: social, economic, and environmental aspects, Biopolym. Ind. Appl. (2021) 351–372, https://doi.org/10.1016/B978-0-12-819240-5.00015-8.
[5] M. Eriksen, L.C.M. Lebreton, H.S. Carson, M. Thiel, C.J. Moore, J.C. Borerro, F. Galgani, P.G. Ryan, J. Reisser, Plastic pollution in the world’s oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea, PLoS One 9 (2014) e111913, https://doi.org/10.1371/JOURNAL.PONE.0111913.
[6] J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, Plastic waste inputs from land into the ocean, Science (1979) 347 (2015) 768–771, https://doi.org/10.1126/SCIENCE.1260352/SUPPL_FILE/JAMBECK.SM.PDF.
[7] D. Hoornweg, P. Bhada-Tata, C. Kennedy, Environment: waste production must peak this century, Nature (2013) 615–617, https://doi.org/10.1038/502615a, 2013 502:7473 502.
[8] S. Anderson, R. Newell, Prospects for carbon capture and storage technologies, Annu. Rev. Environ. Resour. 29 (2004) 109–142, https://doi.org/10.1146/annurev.energy.29.082703.145619.
[9] T.S. Ledley, E.T. Sundquist, S.E. Schwartz, D.K. Hall, J.D. Fellows, T.L. Killeen, Climate change and greenhouse gases, Eos, Trans. Am. Geophys. Union 80 (1999) 453–458, https://doi.org/10.1029/99EO00325.
[10] P. Banerjee, M. Chowdhury, P. Das, A.K. Nadda, A. Mukhopadhayay, Biopolymers for CO2 capture, CO2-Philic polymers, nanocomposites and solvents: capture, Conversion and Industrial Products (2023) 289–320, https://doi.org/10.1016/B978-0-323-85777-2.00011-1.
[11] Q. Al-Yasiri, Gábor Géczi, Global warming potential: causes and consequences, Acad. Lett. 3202 (2021), https://doi.org/10.20935/AL3202.
[12] M.L. Khandekar, T.S. Murty, P. Chittibabu, The global warming debate: a review of the state of science, Pure Appl. Geophys. 162 (2005) 1557–1586, https://doi.org/10.1007/S00024-005-2683-X/METRICS.
[13] L.E. Erickson, G. Brase, Paris agreement on climate change, Reducing Greenh. Gas Emiss. Improv. Air Qual. (2019) 11–22, https://doi.org/10.1201/9781351116589-2.
[14] E. Kabir, R. Kaur, J. Lee, K.H. Kim, E.E. Kwon, Prospects of biopolymer technology as an alternative option for non-degradable plastics and sustainable management of plastic wastes, J. Clean. Prod. 258 (2020) 120536, https://doi.org/10.1016/J.JCLEPRO.2020.120536.
[15] E. Chiellini, P. Cinelli, F. Chiellini, S.H. Imam, Environmentally degradable bio-based polymeric blends and composites, Macromol. Biosci. 4 (2004) 218–231, https://doi.org/10.1002/MABI.200300126.
[16] R.P. Babu, K. O’Connor, R. Seeram, Current progress on bio-based polymers and their future trends, Prog. Biomater. 2 (2013) 8, https://doi.org/10.1186/2194-0517-2-8/TABLES/12.
[17] M.E. González-López, S. de J. Calva-Estrada, M.S. Gradilla-Hernández, P. Barajas-Álvarez, Current trends in biopolymers for food packaging: a review, Front. Sustain. Food Syst. 7 (2023) 1225371, https://doi.org/10.3389/FSUFS.2023.1225371/FULL.
[18] S. Casalini, M. Giacinti Baschetti, The use of essential oils in chitosan or cellulose-based materials for the production of active food packaging solutions: a review, J. Sci. Food Agric. 103 (2023) 1021–1041, https://doi.org/10.1002/JSFA.11918.
[19] V. Siracusa, I. Blanco, Bio-polyethylene (Bio-PE), bio-Polypropylene (Bio-PP) and Bio-poly(ethylene terephthalate) (Bio-PET): recent developments in bio-based polymers analogous to petroleum-derived ones for packaging and engineering applications, Polymers 12 (2020) 1641, https://doi.org/10.3390/POLYM12081641, 2020, Vol. 12, Page 1641.
[20] M. Kolybaba, L.G. Tabil, S. Panigrahi, W.J. Crerar, T. Powell, B. Wang, Biodegradable Polymers: past, Present, and Future, 2006, p. 1, https://doi.org/10.13031/2013.41300.
[21] J. Muller, C. González-Martínez, A. Chiralt, Combination of poly(lactic) acid and starch for biodegradable food packaging, Materials 10 (2017) 952, https://doi.org/10.3390/MA10080952, 10 (2017) 952.
[22] S. Woranuch, A. Pangon, K. Puagsuntia, N. Subjalearndee, V. Intasanta, Starch-based and multi-purpose nanofibrous membrane for high efficiency nanofiltration, RSC Adv. 7 (2017) 35368–35375, https://doi.org/10.1039/C7RA07484K.
[23] P. Grzybek, G. Dudek, B. van der Bruggen, Cellulose-based films and membranes: a comprehensive review on preparation and applications, Chem. Eng. J. 495 (2024) 153500, https://doi.org/10.1016/J.CEJ.2024.153500.
[24] N.A.A.B. Taib, M.R. Rahman, D. Huda, K.K. Kuok, S. Hamdan, M.K. Bin Bakri, M.R.M. Bin Julaihi, A. Khan, A review on poly lactic acid (PLA) as a biodegradable polymer, Polym. Bull. 80 (2023) 1179–1213, https://doi.org/10.1007/S00289-022-04160-Y/TABLES/14.
[25] M. Burelo, J.D. Hernández-Varela, D.I. Medina, C.D. Treviño-Quintanilla, Recent developments in bio-based polyethylene: degradation studies, waste management and recycling, Heliyon 9 (2023) e21374, https://doi.org/10.1016/J.HELIYON.2023.E21374.
[26] R. Kaur, P. Singh, S. Tanwar, G. Varshney, S. Yadav, Assessment of bio-based polyurethanes: perspective on applications and bio-degradation, Macromol 2 (2022) 284–314, https://doi.org/10.3390/MACROMOL2030019, 2 (2022) 284–314.
[27] A. Valdés, A.C. Mellinas, M. Ramos, M.C. Garrigós, A. Jiménez, Natural additives and agricultural wastes in biopolymer formulations for food packaging, Front. Chem. 2 (2014) 79543, https://doi.org/10.3389/FCHEM.2014.00006/BIBTEX.
[28] T.A. Sonia, C.P. Sharma, Chitosan and its derivatives for drug delivery perspective, Adv. Polym. Sci. 243 (2011) 23–53, https://doi.org/10.1007/12_2011_117.
[29] S.D. Gurpreet, K. Surinder, J.S. Saurabh, Recent development in applications of important biopolymer chitosan inbiomedicine, pharmaceuticals and personal care products, Curr. Tissue Eng. 2 (2013) 20–40.
[30] J.C.M. Pires, F.G. Martins, M.C.M. Alvim-Ferraz, M. Simões, Recent developments on carbon capture and storage: an overview, Chem. Eng. Res. Des. 89 (2011) 1446–1460, https://doi.org/10.1016/j.cherd.2011.01.028.

[31] A. Raza, R. Gholami, R. Rezaee, V. Rasouli, M. Rabiei, Significant aspects of carbon capture and storage – a review, Petroleum 5 (2019) 335–340, https://doi.org/10.1016/J.PETLM.2018.12.007.

[32] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, Renew. Sustain. Energy Rev. (2014), https://doi.org/10.1016/j.rser.2014.07.093.

[33] The Intergovernmental Panel on Climate Change (IPCC) Why the IPCC was created, (n.d.).

[34] J. Gibbins, H. Chalmers, Carbon capture and storage, Energy Policy 36 (2008) 4317–4322, https://doi.org/10.1016/j.enpol.2008.09.058.

[35] M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernández, M.C. Ferrari, R. Gross, J.P. Hallett, R. S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R.T.J. Porter, M. Pourkashanian, G.T. Rochelle, N. Shah, J.G. Yao, P.S. Fennell, Carbon capture and storage update, Energy Environ. Sci. 7 (2014) 130–189, https://doi.org/10.1039/c3ee42350f.

[36] H. Herzog, Carbon dioxide capture and storage, in: The Economics and Politics of Climate Change, 2015, https://doi.org/10.1093/acprof:osobl/9780199573288.003.0013.

[37] P. Bernardo, E. Drioli, G. Golemme, Membrane gas separation: a review/state of the art, Ind. Eng. Chem. Res. (2009), https://doi.org/10.1021/ie8019032.

[38] F.M. Baena-Moreno, M. Rodríguez-Galán, F. Vega, B. Alonso-Fariñas, L.F. Vilches Arenas, B. Navarrete, Carbon capture and utilization technologies: a literature review and recent advances, Energy Sources, Part A Recovery, Util. Environ. Eff. 41 (2019) 1403–1433, https://doi.org/10.1080/15567036.2018.1548518.

[39] A. Puleo, D. Paul, S.K.-J. of M. Science, The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate, ElsevierAC puleo, DR Paul, SS KelleyJournal of Membr. Sci., 1989•Elsevier (1989) undefined.

[40] G.Q. Chen, S. Kanehashi, C.M. Doherty, A.J. Hill, S.E. Kentish, Water vapor permeation through cellulose acetate membranes and its impact upon membrane separation performance for natural gas purification, J. Membr. Sci. 487 (2015) 249–255, https://doi.org/10.1016/J.MEMSCI.2015.03.074.

[41] M. Mubashir, L.F. Dumée, Y.Y. Fong, N. Jusoh, J. Lukose, W.S. Chai, P.L. Show, Cellulose acetate-based membranes by interfacial engineering and integration of ZIF-62 glass nanoparticles for CO2 separation, J. Hazard Mater. 415 (2021) 1–10, https://doi.org/10.1016/J.JHAZMAT.2021.125639, 125639.

[42] H. Sanaeepur, A. Kargari, B. Nasernejad, A. Ebadi Amooghin, M. Omidkhah, A novel Co2+ exchanged zeolite Y/cellulose acetate mixed matrix membrane for CO2/N2 separation, J. Taiwan Inst. Chem. Eng. 60 (2016) 403–413, https://doi.org/10.1016/J.JTICE.2015.10.042.

[43] A.R. Moghadassi, Z. Rajabi, S.M. Hosseini, M. Mohammadi, Fabrication and modification of cellulose acetate based mixed matrix membrane: gas separation and physical properties, J. Ind. Eng. Chem. 20 (2014) 1050–1060, https://doi.org/10.1016/J.JIEC.2013.06.042.

[44] A.L. Ahmad, Z.A. Jawad, S.C. Low, S.H.S. Zein, A cellulose acetate/multi-walled carbon nanotube mixed matrix membrane for CO2/N2 separation, J. Membr. Sci. 451 (2014) 55–66, https://doi.org/10.1016/J.MEMSCI.2013.09.043.

[45] M. Najafi, M. Sadeghi, A. Bolverdi, M. Pourafshari Chenar, M. Pakizeh, Gas permeation properties of cellulose acetate/silica nanocomposite membrane, Adv. Polym. Technol. 37 (2018) 2043–2052, https://doi.org/10.1002/ADV.21862.

[46] H. Sanaeepur, R. Ahmadi, M. Sinaei, A. Kargari, Pebax-modified cellulose acetate membrane for CO2/N2 separation, J. Membr. Sci. Res. 5 (2019) 25–32, https://doi.org/10.22079/JMSR.2018.85813.1190.

[47] E. Akbarzadeh, A. Shockravi, V. Vatanpour, High performance compatible thiazole-based polymeric blend cellulose acetate membrane as selective CO2 absorbent and molecular sieve, Carbohydr. Polym. 252 (2021) 117215, https://doi.org/10.1016/J.CARBPOL.2020.117215.

[48] A. Raza, S. Farrukh, A. Hussain, I.U. Khan, T. Noor, M.H.D. Othman, M.F. Yousaf, Development of high performance amine functionalized zeolitic imidazolate framework (ZIF-8)/cellulose triacetate mixed matrix membranes for CO2/CH4 separation, Int. J. Energy Res. 44 (2020) 7989–7999, https://doi.org/10.1002/ER.5448.

[49] X.G. Li, I. Kresse, Z.K. Xu, J. Springer, Effect of temperature and pressure on gas transport in ethyl cellulose membrane, Polymer (Guildf.) 42 (2001) 6801–6810, https://doi.org/10.1016/S0032-3861(01)00121-5.

[50] K. Yang, Y. Dai, W. Zheng, X. Ruan, H. Li, G. He, ZIFs-modified GO plates for enhanced CO2 separation performance of ethyl cellulose based mixed matrix membranesf, Sep. Purif. Technol. 214 (2019) 87–94, https://doi.org/10.1016/J.SEPPUR.2018.04.080.

[51] L. Ansaloni, J. Salas-Gay, S. Ligi, M.G. Baschetti, Nanocellulose-based membranes for CO2 capture, J. Membr. Sci. 522 (2017) 216–225, https://doi.org/10.1016/J.MEMSCI.2016.09.024.

[52] D. Venturi, D. Grupkovic, L. Sisti, M.G. Baschetti, Effect of humidity and nanocellulose content on Polyvinylamine-nanocellulose hybrid membranes for CO2 capture, J. Membr. Sci. 548 (2018) 263–274, https://doi.org/10.1016/J.MEMSCI.2017.11.021.

[53] D. Venturi, A. Chrysanthou, B. Dhuiège, K. Missoum, M.G. Baschetti, Arginine/nanocellulose membranes for carbon capture applications, Nanomaterials 9 (2019) 877, https://doi.org/10.3390/NANO9060877, 2019, Vol. 9, Page 877.

[54] R. Casadei, E. Firouznia, M.G. Baschetti, Effect of Mobile carrier on the performance of PVAm–Nanocellulose facilitated transport membranes for CO2 capture, Membranes 11 (2021) 442, https://doi.org/10.3390/MEMBRANES11060442, 2021, Vol. 11, Page 442.

[55] B. Dhuiège, E. Lasseuguette, M.C. Brochier-Salon, M.C. Ferrari, K. Missoum, Crosslinked facilitated transport membranes based on carboxymethylated NFC and amine-based fixed carriers for carbon capture, utilization, and storage applications, Appl. Sci. 10 (2020) 414, https://doi.org/10.3390/APP10010414, 2020, Vol. 10, Page 414.

[56] S. Janakiram, L. Ansaloni, S.A. Jin, X. Yu, Z. Dai, R.J. Spontak, L. Deng, Humidity-responsive molecular gate-opening mechanism for gas separation in ultraselective nanocellulose/IL hybrid membranes, Green Chem. 22 (2020) 3546–3557, https://doi.org/10.1039/D0GC00544D.

[57] I. Pylypchuk, R. Selyanchyn, T. Budnyak, Y. Zhao, M. Lindström, S. Fujikawa, O. Sevastyanova, “Artificial Wood” lignocellulosic membranes: influence of kraft lignin on the properties and gas transport in tunicate-based nanocellulose composites, Membranes 11 (2021) 204, https://doi.org/10.3390/MEMBRANES11030204, 2021, Vol. 11, Page 204.

[58] M. Jia, X.F. Zhang, Y. Feng, Y. Zhou, J. Yao, In-situ growing ZIF-8 on cellulose nanofibers to form gas separation membrane for CO2 separation, J. Membr. Sci. 595 (2020) 117579, https://doi.org/10.1016/J.MEMSCI.2019.117579.

[59] X.F. Zhang, Y. Feng, Z. Wang, M. Jia, J. Yao, Fabrication of cellulose nanofibrils/UiO-66-NH2 composite membrane for CO2/N2 separation, J. Membr. Sci. 568 (2018) 10–16, https://doi.org/10.1016/J.MEMSCI.2018.09.055.

[60] S. Janakiram, X. Yu, L. Ansaloni, Z. Dai, L. Deng, Manipulation of fibril surfaces in nanocellulose-based facilitated transport membranes for enhanced CO2 capture, ACS Appl. Mater. Interfaces 11 (2019) 33302–33313, https://doi.org/10.1021/ACSAMI.9B09920/SUPPL_FILE/AM9B09920_SI_001.PDF.

[61] Z. Dai, J. Deng, Q. Yu, R.M.L. Helberg, S. Janakiram, L. Ansaloni, L. Deng, Fabrication and evaluation of bio-based nanocomposite TFC hollow fiber membranes for enhanced CO 2 capture, ACS Appl. Mater. Interfaces 11 (2019) 10874–10882, https://doi.org/10.1021/ACSAMI.8B19651/ASSET/IMAGES/LARGE/AM-2018-19651N_0009.JPEG.

[62] Z. Jahan, M.B.K. Niazi, M.B. Hägg, Ø.W. Gregersen, Cellulose nanocrystal/PVA nanocomposite membranes for CO2/CH4 separation at high pressure, J. Membr. Sci. 554 (2018) 275–281, https://doi.org/10.1016/J.MEMSCI.2018.02.061.

[63] J. Torstensen, R.M.L. Helberg, L. Deng, Ø.W. Gregersen, K. Syverud, PVA/nanocellulose nanocomposite membranes for CO2 separation from flue gas, Int. J. Greenh. Gas Control 81 (2019) 93–102, https://doi.org/10.1016/J.IJGGC.2018.10.007.

[64] R.M.L. Helberg, J. Torstensen, Z. Dai, S. Janakiram, G. Chinga-Carrasco, Ø. W. Gregersen, K. Syverud, L. Deng, Nanocomposite membranes with high-charge and size-screened phosphorylated nanocellulose fibrils for CO2 separation, Green Energy Environ. 6 (2021) 585–596, https://doi.org/10.1016/J.GEE.2020.08.004.

[65] S. Nithin Mithra, S.S. Ahankari, Phosphorylated cellulose nanocrystals/polyvinyl alcohol-L arginine coating in facilitated transport membranes for biogas purification, Carbohydr. Polym. Technol. Appli. 9 (2025) 100679, https://doi.org/10.1016/J.CARPTA.2025.100679.

[66] N. Mithra S, S.S. Ahankari, The synergistic effect of carboxymethylated cellulose nanocrystals -Polyvinyl alcohol- L arginine in facilitated transport membranes for biogas purification, J. Ind. Eng. Chem. 144 (2025) 782–791, https://doi.org/10.1016/J.JIEC.2024.12.033.

[67] Z. Dai, J. Deng, Y. Ma, H. Guo, J. Wei, B. Wang, X. Jiang, L. Deng, Nanocellulose crystal-enhanced hybrid membrane for CO2Capture, Ind. Eng. Chem. Res. 61 (2022) 9067–9076, https://doi.org/10.1021/ACS.IECR.2C01402/ASSET/IMAGES/MEDIUM/IE2C01402_0012.GIF.

[68] S. Nilouyal, H.E. Karahan, A.P. Isfahani, D. Qin, M.M. Ito, E. Sivaniah, B. Ghalei, Nanocellulose-Incorporated composite membranes of PEO-based rubbery polymers for carbon dioxide capture, Adv. Polym. Technol. 2024 (2024) 6697045, https://doi.org/10.1155/2024/6697045.

[69] A. Ito, M. Sato, T. Anma, Permeability of CO2 through chitosan membrane swollen by water vapor in feed gas, Die Angewandte Makromolekulare Chemie 248 (1997) 85–94, https://doi.org/10.1002/APMC.1997.052480105.

[70] L.A. El-Azzami, E.A. Grulke, Carbon dioxide separation from hydrogen and nitrogen by fixed facilitated transport in swollen chitosan membranes, J. Membr. Sci. 323 (2008) 225–234, https://doi.org/10.1016/J.MEMSCI.2008.05.019.

[71] L.A. El-Azzami, E.A. Grulke, Carbon dioxide separation from hydrogen and nitrogen: facilitated transport in arginine salt–chitosan membranes, J. Membr. Sci. 328 (2009) 15–22, https://doi.org/10.1016/J.MEMSCI.2008.08.038.

[72] R. Borgohain, B. Prasad, B. Mandal, Synthesis and characterization of water-soluble chitosan membrane blended with a mobile carrier for CO2 separation, Sep. Purif. Technol. 222 (2019) 177–187, https://doi.org/10.1016/J.SEPPUR.2019.04.038.

[73] R. Borgohain, B. Mandal, PH responsive carboxymethyl chitosan/poly(amidoamine) molecular gate membrane for CO2/N2 separation, ACS Appl. Mater. Interfaces 11 (2019) 42616–42628, https://doi.org/10.1021/ACSAMI.9B15044/SUPPL_FILE/AM9B15044_SI_001.PDF.

[74] R. Borgohain, B. Mandal, Thermally stable and moisture responsive carboxymethyl chitosan/dendrimer/hydrotalcite membrane for CO2 separation, J. Membr. Sci. 608 (2020) 118214, https://doi.org/10.1016/J.MEMSCI.2020.118214.

[75] J.N. Shen, C.C. Yu, G.N. Zeng, B. van der Bruggen, Preparation of a facilitated transport membrane composed of carboxymethyl chitosan and polyethylenimine for CO2/N2 separation, Int. J. Mol. Sci. 14 (2013) 3621–3638, https://doi.org/10.3390/IJMS14023621, 14 (2013) 3621–3638.

[76] B. Prasad, B. Mandal, Moisture responsive and CO2 selective biopolymer membrane containing silk fibroin as a green carrier for facilitated transport of CO2, J. Membr. Sci. 550 (2018) 416–426, https://doi.org/10.1016/J.MEMSCI.2017.12.061.

[77] E. Santos, E. Rodríguez-Fernández, C. Casado-Coterillo, Á. Irabien, Hybrid ionic liquid-chitosan membranes for CO2 separation: mechanical and thermal behavior, Int. J. Chem. React. Eng. 14 (2016) 713–718, https://doi.org/10.1515/IJCRE-2014-0109/MACHINEREADABLECITATION/RIS.

[78] A. Katare, R. Borgohain, B. Prasad, B. Mandal, A strategical improvement in the performance of CO2/N2 gas permeation via conjugation of L-Tyrosine onto chitosan membrane, Membranes 13 (2023) 487, https://doi.org/10.3390/MEMBRANES13050487/S1.

[79] A. Katare, S. Sharma, H. Horo, S. Bhowmick, L.M. Kundu, B. Mandal, An investigation on the effects of both amine grafting and blending with biodegradable chitosan membrane for CO2 capture from CO2/N2 gas mixtures, Chem. Eng. J. 466 (2023) 143215, https://doi.org/10.1016/J.CEJ.2023.143215.

[80] Y. Shen, H. Wang, J. Liu, Y. Zhang, Enhanced performance of a novel polyvinyl amine/chitosan/graphene oxide mixed matrix membrane for CO2 capture, ACS Sustain. Chem. Eng. 3 (2015) 1819–1829, https://doi.org/10.1021/ACSSUSCHEMENG.5B00409/ASSET/IMAGES/LARGE/SC-2015-00409Z_0014.JPEG.

[81] A. Iulianelli, F. Russo, F. Galiano, G. Desiderio, A. Basile, A. Figoli, PLA Easy fil – White-based membranes for CO2 separation, Greenh. Gases: Sci. Technol. 9 (2019) 360–369, https://doi.org/10.1002/GHG.1853.

[82] A. Iulianelli, C. Algieri, L. Donato, A. Garofalo, F. Galiano, G. Bagnato, A. Basile, A. Figoli, New PEEK-WC and PLA membranes for H2 separation, Int. J. Hydrogen Energy 42 (2017) 22138–22148, https://doi.org/10.1016/J.IJHYDENE.2017.04.060.

[83] A. Iulianelli, F. Russo, F. Galiano, M. Manisco, A. Figoli, Novel bio-polymer based membranes for CO2/CH4 separation, Int. J. Greenh. Gas Control 117 (2022) 103657, https://doi.org/10.1016/J.IJGGC.2022.103657.

[84] R. Checchetto, M. Scarpa, M.G. De Angelis, M. Minelli, Mixed gas diffusion and permeation of ternary and quaternary CO2/CO/N2/O2 gas mixtures in matrimid®, polyetherimide and poly(lactic acid) membranes for CO2/CO separation, J. Membr. Sci. 659 (2022) 120768, https://doi.org/10.1016/J.MEMSCI.2022.120768.

[85] S. Saedi, S.S. Madaeni, F. Seidi, A.A. Shamsabadi, S. Laki, Synthesis and application of a novel Amino-starch derivative as a new polymeric additive for fixed facilitated transport of carbon dioxide through an asymmetric polyethersulfone (PES) membrane, Int. J. Greenh. Gas Control 19 (2013) 126–137, https://doi.org/10.1016/J.IJGGC.2013.06.019.

[86] V. Vatanpour, M.E. Pasaoglu, H. Barzegar, O.O. Teber, R. Kaya, M. Bastug, A. Khataee, I. Koyuncu, Cellulose acetate in fabrication of polymeric membranes: a review, Chemosphere 295 (2022) 133914, https://doi.org/10.1016/J.CHEMOSPHERE.2022.133914.

[87] A.M. Vijesh, A.M. Isloor, Review on polymeric membrane materials for gas separations which are stated above the Robeson's trade-off upper bound, Curr. TrendsFuture Dev. (Bio-) Membr.: Mod. Approach. Membrane Technol. Gas Separ. Water Treat. (2024) 3–28, https://doi.org/10.1016/B978-0-323-99311-1.00005-2.

[88] P. Pandey, R.S. Chauhan, Membranes for gas separation, Prog. Polym. Sci. 26 (2001) 853–893, https://doi.org/10.1016/S0079-6700(01)00009-0.

[89] K. Ghosal, B.D. Freeman, Gas separation using polymer membranes: an overview, Polym. Adv. Technol. 5 (1994) 673–697, https://doi.org/10.1002/PAT.1994.220051102.

[90] R.W. Baker, B.T. Low, Gas separation membrane materials: a perspective, Macromolecules 47 (2014) 6999–7013, https://doi.org/10.1021/MA501488S/ASSET/IMAGES/LARGE/MA-2014-01488S_0017.JPEG.

[91] L. Ansaloni, L. Deng, Advances in polymer-inorganic hybrids as membrane materials, in: Recent Developments in Polymer Macro, Micro and Nano Blends: Preparation and Characterisation, 2017, https://doi.org/10.1016/B978-0-08-100408-1.00007-8.

[92] J.G. Wijmans, R.W. Baker, The solution-diffusion model: a review, J. Membr. Sci. 107 (1995) 1–21, https://doi.org/10.1016/0376-7388(95)00102-I.

[93] Y. Yampolskii, B.D. Freeman, I. Pinnau, S. Matteucci, Transport of gases and vapors in glassy and rubbery polymers., Mater. Sci. Membranes Gas Vapor Separation (n.d.) 1–47. doi: 10.1002/047002903X.

[94] K.A. Lokhandwala, R.W. Baker, K.D. Amo, Sour Gas Treatment Process, 1995.

[95] R.W. Baker, Membrane technology and applications. https://doi.org/10.1002/9781118359686, 2012.

[96] L.M. Robeson, Polymeric membranes for gas separation, in: Encyclopedia of Materials: Science and Technology, 2001, https://doi.org/10.1016/b0-08-043152-6/01364-4.

[97] B.D. Freeman, Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, Macromolecules 32 (1999) 375–380, https://doi.org/10.1021/MA9814548/ASSET/IMAGES/MEDIUM/MA9814548E00017.GIF.

[98] R. Selyanchyn, S. Fujikawa, Membrane thinning for efficient CO2 capture, Sci. Technol. Adv. Mater. 18 (2017) 816–827, https://doi.org/10.1080/14686996.2017.1386531/ASSET/C5C9A471-4E8C-4E65-92DB-D75176672BA8/ASSETS/IMAGES/LARGE/TSTA_A_1386531_F0008_OC.JPG.

[99] L.M. Robeson, Polymeric membranes for gas separation, in: Reference Module in Materials Science and Materials Engineering, 2016, https://doi.org/10.1016/b978-0-12-803581-8.03297-5.

[100] L.M. Robeson, Polymer membranes for gas separation, Curr. Opin. Solid State Mater. Sci. (1999). https://doi.org/10.1016/S1359-0286(00)00014-0.

[101] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci. 62 (1991) 165–185, https://doi.org/10.1016/0376-7388(91)80060-J.

[102] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390–400, https://doi.org/10.1016/J.MEMSCI.2008.04.030.

[103] L.M. Robeson, B.D. Freeman, D.R. Paul, B.W. Rowe, An empirical correlation of gas permeability and permselectivity in polymers and its theoretical basis, J. Membr. Sci. 341 (2009) 178–185, https://doi.org/10.1016/J.MEMSCI.2009.06.005.

[104] B. Comesaña-Gándara, J. Chen, C.G. Bezzu, M. Carta, I. Rose, M.C. Ferrari, E. Esposito, A. Fuoco, J.C. Jansen, N.B. McKeown, Redefining the robeson upper bounds for CO2/CH4 and CO2/N2 separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity, Energy Environ. Sci. 12 (2019) 2733–2740, https://doi.org/10.1039/c9ee01384a.

[105] Y. Wang, Y. Zhou, X. Zhang, Y. Gao, J. Li, SPEEK membranes by incorporation of NaY zeolite for CO2/N2 separation, Sep. Purif. Technol. 275 (2021) 119189, https://doi.org/10.1016/J.SEPPUR.2021.119189.

[106] J. Liu, X. Hou, H.B. Park, H. Lin, High-performance polymers for membrane CO2/N2 separation, Chem. Eur J. 22 (2016) 15980–15990, https://doi.org/10.1002/CHEM.201603002.

[107] H.Z. Chen, Z. Thong, P. Li, T.S. Chung, High performance composite hollow fiber membranes for CO2/H2 and CO2/N2 separation, Int. J. Hydrogen Energy 39 (2014) 5043–5053, https://doi.org/10.1016/J.IJHYDENE.2014.01.047.

[108] C.E. Powell, G.G. Qiao, Polymeric CO2/N2 gas separation membranes for the capture of carbon dioxide from power plant flue gases, J. Membr. Sci. 279 (2006) 1–49, https://doi.org/10.1016/J.MEMSCI.2005.12.062.

[109] M. Chawla, H. Saulat, M. Masood Khan, M. Mahmood Khan, S. Rafiq, L. Cheng, T. Iqbal, M.I. Rasheed, M.Z. Farooq, M. Saeed, N.M. Ahmad, M.B. Khan Niazi, S. Saqib, F. Jamil, A. Mukhtar, N. Muhammad, Membranes for CO2/CH4 and CO2/N2 gas separation, Chem. Eng. Technol. 43 (2020) 184–199, https://doi.org/10.1002/CEAT.201900375;WGROUP:STRING:PUBLICATION.

[110] N.A.D. Ho, C.P. Leo, A review on the emerging applications of cellulose, cellulose derivatives and nanocellulose in carbon capture, Environ. Res. 197 (2021) 111100, https://doi.org/10.1016/J.ENVRES.2021.111100.

[111] D.D. Iarikov, S. Ted Oyama, Review of CO2/CH4 separation membranes, Membr. Sci. Technol. 14 (2011) 91–115, https://doi.org/10.1016/B978-0-444-53728-7.00005-7.

[112] Y.W. Jeon, D.H. Lee, Gas membranes for CO2/CH4 (biogas) separation, A Review 32 (2015) 71–85, https://doi.org/10.1089/EES.2014.0413. https://Home.Liebertpub.Com/Ees.

[113] S. Elhenawy, M. Khraisheh, F. AlMomani, M. Hassan, Key applications and potential limitations of ionic liquid membranes in the gas separation process of CO2, CH4, N2, H2 or mixtures of these gases from various gas streams, Molecules 25 (2020) 4274, https://doi.org/10.3390/MOLECULES25184274, 2020, Vol. 25, Page 4274.

[114] X. Zhang, Z. Tu, H. Li, K. Huang, X. Hu, Y. Wu, D.R. MacFarlane, Selective separation of H2S and CO2 from CH4 by supported ionic liquid membranes, J. Membr. Sci. 543 (2017) 282–287, https://doi.org/10.1016/J.MEMSCI.2017.08.033.

[115] L. Olivieri, H. Aboukeila, M. Giacinti Baschetti, D. Pizzi, L. Merlo, G.C. Sarti, Humid permeation of CO2 and hydrocarbons in aquivion® perfluorosulfonic acid ionomer membranes, experimental and modeling, J. Membr. Sci. (2017), https://doi.org/10.1016/j.memsci.2017.08.030.

[116] M. Isanejad, N. Azizi, T. Mohammadi, Pebax membrane for CO2/CH4 separation: effects of various solvents on morphology and performance, J. Appl. Polym. Sci. 134 (2017), https://doi.org/10.1002/APP.44531.

[117] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: an overview, Ind. Eng. Chem. Res. 47 (2008) 2109–2121, https://doi.org/10.1021/IE071083W.

[118] Y. Yang, Y. Han, B. Prasad, R. Pang, C. Zou, W.S.W. Ho, Carbon capture from flue gases using an integrated membrane skid, J. Membr. Sci. 718 (2025) 123674, https://doi.org/10.1016/J.MEMSCI.2024.123674.

[119] T. Merkel, J. Kniep, X. Wei, T. Carlisle, S. White, S. Pande, D. Fulton, R. Watson, T. Hoffman, B. Freeman, R. Baker, Pilot testing of a membrane system for postcombustion CO2 capture. https://doi.org/10.2172/1337555, 2015.

[120] Richard D. Noble, C.A. Koval, Review of facilitated transport membranes, Membranes Gas Vapor Separ. (2006) 411–425.

[121] R. Rea, M.G. De Angelis, M.G. Baschetti, Models for facilitated transport membranes: a review, Membranes 9 (2019) 26, https://doi.org/10.3390/MEMBRANES9020026, 2019, Vol. 9, Page 26.

[122] E. Lasseuguette, M.C. Ferrari, Polymer membranes for sustainable gas separation, Sustain. Nano. Eng.: Mater Des. Chem. Process. (2020) 265–296, https://doi.org/10.1016/B978-0-12-814681-1.00010-2.

[123] M. Caplow, Kinetics of carbamate Formation and breakdown, J. Am. Chem. Soc. 90 (1968) 6795–6803, https://doi.org/10.1021/ja01026a041.

[124] A. Eisenberg, Clustering of ions in organic polymers. A theoretical approach, Macromolecules (1970), https://doi.org/10.1021/ma60014a006.

[125] R. Casadei, D. Venturi, M.G. Baschetti, L. Giorgini, E. Maccaferri, S. Ligi, Polyvinylamine membranes containing Graphene-based nanofillers for carbon capture applications, Membranes 9 (2019) 119, https://doi.org/10.3390/MEMBRANES9090119, 2019, Vol. 9, Page 119.

[126] S. Zeng, X. Zhang, L. Bai, X. Zhang, H. Wang, J. Wang, D. Bao, M. Li, X. Liu, S. Zhang, Ionic-Liquid-based CO2 capture systems: structure, interaction and process, Chem. Rev. 117 (2017) 9625–9673, https://doi.org/10.1021/acs.chemrev.7b00072.

[127] S. Babamohammadi, A. Shamiri, M.K. Aroua, A review of CO2 capture by absorption in ionic liquid-based solvents, Rev. Chem. Eng. 31 (2015) 383–412, https://doi.org/10.1515/revce-2014-0032.

[128] T.L. Greaves, C.J. Drummond, Protic ionic liquids: properties and applications, Chem. Rev. 108 (2008) 206–237, https://doi.org/10.1021/cr068040u.

[129] J. Liu, S. Zhang, D. en Jiang, C.M. Doherty, A.J. Hill, C. Cheng, H.B. Park, H. Lin, Highly polar but amorphous polymers with robust membrane CO2/N2 separation performance, Joule 3 (2019) 1881–1894, https://doi.org/10.1016/J.JOULE.2019.07.003/ATTACHMENT/FDB14C23-F406-4BED-AC82-605E8CCD4C1F/MMC2.PDF.

[130] Y. Han, W.S.W. Ho, Polymeric membranes for CO2 separation and capture, J. Membr. Sci. 628 (2021) 119244, https://doi.org/10.1016/J.MEMSCI.2021.119244.

[131] S.H. Han, Y.M. Lee, Recent High Performance Polymer Membranes for CO2 Separation, 2011, pp. 84–124, https://doi.org/10.1039/9781849733472-00084.

[132] P. Madejski, K. Chmiel, N. Subramanian, T. Kuś, Methods and techniques for CO2 capture: review of potential solutions and applications in modern energy technologies, Energies 15 (2022) 887, https://doi.org/10.3390/EN15030887, 2022, Vol. 15, Page 887.

[133] C.A. Scholes, K.H. Smith, S.E. Kentish, G.W. Stevens, CO2 capture from pre-combustion processes—Strategies for membrane gas separation, Int. J. Greenh. Gas Control 4 (2010) 739–755, https://doi.org/10.1016/J.IJGGC.2010.04.001.

[134] S. Wickramanayake, D. Hopkinson, C. Myers, L. Sui, D. Luebke, Investigation of transport and mechanical properties of hollow fiber membranes containing ionic liquids for pre-combustion carbon dioxide capture, J. Membr. Sci. 439 (2013) 58–67, https://doi.org/10.1016/J.MEMSCI.2013.03.039.

[135] A. Iulianelli, A. Basile, H. Li, R.W. Van den Brink, Inorganic membranes for pre-combustion carbon dioxide (CO2) capture, Adv. Membrane Sci. Technol. Sustainable Energy Environ. Appl. (2011) 184–213, https://doi.org/10.1533/9780857093790.2.184.

[136] Z.M. Xia, X. Sen Li, Z.Y. Chen, G. Li, K.F. Yan, C.G. Xu, Q.N. Lv, J. Cai, Hydrate-based CO2 capture and CH4 purification from simulated biogas with synergic additives based on gas solvent, Appl. Energy 162 (2016) 1153–1159, https://doi.org/10.1016/J.APENERGY.2015.02.016.

[137] X.Y. Chen, H. Vinh-Thang, A.A. Ramirez, D. Rodrigue, S. Kaliaguine, Membrane gas separation technologies for biogas upgrading, RSC Adv. 5 (2015) 24399–24448, https://doi.org/10.1039/C5RA00666J.

[138] H. Lin, E. Van Wagner, R. Raharjo, B.D. Freeman, I. Roman, High-performance polymer membranes for natural-gas sweetening, Adv. Mater. 18 (2006) 39–44, https://doi.org/10.1002/adma.200501409.

[139] J. Haider, S. Saeed, M.A. Qyyum, B. Kazmi, R. Ahmad, A. Muhammad, M. Lee, Simultaneous capture of acid gases from natural gas adopting ionic liquids: challenges, recent developments, and prospects, Renew. Sustain. Energy Rev. 123 (2020) 109771, https://doi.org/10.1016/j.rser.2020.109771.

[140] C.A. Scholes, G.W. Stevens, S.E. Kentish, Membrane gas separation applications in natural gas processing, Fuel 96 (2012) 15–28, https://doi.org/10.1016/J.FUEL.2011.12.074.

[141] Energy Information Administration, Natural Gas Processing : the Crucial Link Between Natural Gas Production and its Transportation to Market, 2006, pp. 1–11.

[142] A. Pudi, M. Rezaei, V. Signorini, M.P. Andersson, M.G. Baschetti, S.S. Mansouri, Hydrogen sulfide capture and removal technologies: a comprehensive review of recent developments and emerging trends, Sep. Purif. Technol. 298 (2022) 121448, https://doi.org/10.1016/J.SEPPUR.2022.121448.

[143] L.Y. Wang, Y.L. Xu, Z.D. Li, Y.N. Wei, J.P. Wei, CO2/CH4 and H2S/CO2 selectivity by ionic liquids in natural gas sweetening, Energy Fuels 32 (2018) 10–23, https://doi.org/10.1021/acs.energyfuels.7b02852.

[144] C. Chiappe, C.S. Pomelli, Hydrogen sulfide and ionic liquids: absorption, separation, and oxidation, Top. Curr. Chem. 375 (2017) 1–25, https://doi.org/10.1007/s41061-017-0140-9.

[145] D.R. Pesiri, B. Jorgensen, R.C. Dye, Thermal optimization of polybenzimidazole meniscus membranes for the separation of hydrogen, methane, and carbon dioxide, J. Membr. Sci. 218 (2003) 11–18, https://doi.org/10.1016/S0376-7388(03)00129-7.

[146] N. Haimour, O.C. Sand All, Selective removal of hydrogen sulfide from gases containing hydrogen sulfide and carbon dioxide using diethanolamine, Separ. Sci. Technol. 18 (1983) 1221–1249, https://doi.org/10.1080/01496398308059925.

[147] E. Martínez-Pañeda, A. Golahmar, C.F. Niordson, A phase field formulation for hydrogen assisted cracking, Comput. Methods Appl. Mech. Eng. 342 (2018) 742–761, https://doi.org/10.1016/J.CMA.2018.07.021.

[148] F. Kadirkhan, P.S. Goh, A.F. Ismail, W.N.F. Wan Mustapa, M.H.M. Halim, W. K. Soh, S.Y. Yeo, Recent advances of polymeric membranes in tackling plasticization and aging for practical industrial CO2/CH4 applications—A review, Membranes 12 (2022) 71, https://doi.org/10.3390/MEMBRANES12010071, 2022, Vol. 12, Page 71.

[149] N. Alaslai, B. Ghanem, F. Alghunaimi, E. Litwiller, I. Pinnau, Pure- and mixed-gas permeation properties of highly selective and plasticization resistant hydroxyl-diamine-based 6FDA polyimides for CO2/CH4 separation, J. Membr. Sci. 505 (2016) 100–107, https://doi.org/10.1016/J.MEMSCI.2015.12.053.

[150] T. Visser, N. Masetto, M. Wessling, Materials dependence of mixed gas plasticization behavior in asymmetric membranes, J. Membr. Sci. 306 (2007) 16–28, https://doi.org/10.1016/J.MEMSCI.2007.07.048.

[151] G. Dong, H. Li, V. Chen, Factors affect defect-free matrimid® hollow fiber gas separation performance in natural gas purification, J. Membr. Sci. 353 (2010) 17–27, https://doi.org/10.1016/J.MEMSCI.2010.02.012.

[152] L. Olivieri, R. Trichkov, D. Pizzi, L. Merlo, M.G. Baschetti, The effect of pressure and mixed gas composition on humid CO2 and hydrocarbons permeation in aquivion® PFSA, J. Membr. Sci. (2018), https://doi.org/10.1016/j.memsci.2018.08.048.

[153] Z. Dai, H. Aboukeila, L. Ansaloni, J. Deng, M. Giacinti Baschetti, L. Deng, Nafion/PEG hybrid membrane for CO2 separation: effect of PEG on membrane micro-structure and performance, Sep. Purif. Technol. (2019), https://doi.org/10.1016/j.seppur.2018.03.062.

[154] M. Giacinti Baschetti, M. Minelli, J. Catalano, G.C. Sarti, Gas permeation in perflurosulfonated membranes: influence of temperature and relative humidity, Int. J. Hydrogen Energy (2013), https://doi.org/10.1016/j.ijhydene.2013.06.104.

[155] V. Signorini, M. Giacinti Baschetti, D. Pizzi, L. Merlo, Permeation of ternary mixture containing H2S, CO2 and CH4 in aquivion® perfluorosulfonic acid (PFSA) ionomer membranes, Membranes 12 (2022) 1034, https://doi.org/10.3390/MEMBRANES12111034, 2022, Vol. 12, Page 1034.

[156] T.C. Merkel, L.G. Toy, Comparison of hydrogen sulfide transport properties in fluorinated and nonfluorinated polymers, Macromolecules (2006), https://doi.org/10.1021/ma061072z.

[157] J. Pellegrino, Y.S. Kang, CO2 CH4 transport in polyperfluorosulfonate ionomers: effects of polar solvents on permeation and solubility, J. Membr. Sci. 99 (1995) 163–174, https://doi.org/10.1016/0376-7388(94)00211-G.

[158] J.H. Petropoulos, Mechanisms and theories for sorption and diffusion of gases in polymers, Polym Gas Separ. Membr. (2018) 17–81, https://doi.org/10.1201/9781351075886-2.

[159] C.A. Scholes, G.W. Stevens, S.E. Kentish, The effect of hydrogen sulfide, carbon monoxide and water on the performance of a PDMS membrane in carbon dioxide/nitrogen separation, J. Membr. Sci. 350 (2010) 189–199, https://doi.org/10.1016/j.memsci.2009.12.027.

[160] S. Choi, J. Coronas, Z. Lai, D. Yust, F. Onorato, M. Tsapatsis, Fabrication and gas separation properties of polybenzimidazole (PBI)/nanoporous silicates hybrid membranes, J. Membr. Sci. 316 (2008) 145–152, https://doi.org/10.1016/J.MEMSCI.2007.09.026.

[161] S.S. Hosseini, M.M. Teoh, T.S. Chung, Hydrogen separation and purification in membranes of miscible polymer blends with interpenetration networks, Polymer (Guildf.) 49 (2008) 1594–1603, https://doi.org/10.1016/J.POLYMER.2008.01.052.

[162] H. Lin, B.D. Freeman, Materials selection guidelines for membranes that remove CO2 from gas mixtures, J. Mol. Struct. 739 (2005) 57–74, https://doi.org/10.1016/J.MOLSTRUC.2004.07.045.

[163] T.C. Merkel, R.P. Gupta, B.S. Turk, B.D. Freeman, Mixed-gas permeation of syngas components in poly(dimethylsiloxane) and poly(1-trimethylsilyl-1-propyne) at elevated temperatures, J. Membr. Sci. 191 (2001) 85–94, https://doi.org/10.1016/S0376-7388(01)00452-5.

[164] E. Lasseuguette, M.C. Ferrari, S. Brandani, Humidity impact on the gas permeability of PIM-1 membrane for post-combustion application, Energy Proc. 63 (2014) 194–201, https://doi.org/10.1016/J.EGYPRO.2014.11.020.

[165] L.M. Robeson, M.E. Dose, B.D. Freeman, D.R. Paul, Analysis of the transport properties of thermally rearranged (TR) polymers and polymers of intrinsic microporosity (PIM) relative to upper bound performance, J. Membr. Sci. 525 (2017) 18–24, https://doi.org/10.1016/J.MEMSCI.2016.11.085.

[166] L.E. Starannikova, A.Y. Alentiev, R.Y. Nikiforov, I.I. Ponomarev, I. V. Blagodatskikh, A.Y. Nikolaev, V.P. Shantarovich, Y.P. Yampolskii, Effects of different treatments of films of PIM-1 on its gas permeation parameters and free volume, Polymer (Guildf.) 212 (2021) 123271, https://doi.org/10.1016/J.POLYMER.2020.123271.

[167] M. Giacinti Baschetti, F. Doghieri, B. Freeman, G.C. Sarti, Transient and steady-state effective diffusivity in high free volume glassy polymers, J. Membr. Sci. 344 (2009) 144–154, https://doi.org/10.1016/J.MEMSCI.2009.07.045.

[168] Y. Huang, X. Wang, D.R. Paul, Physical aging of thin glassy polymer films: free volume interpretation, J. Membr. Sci. 277 (2006) 219–229, https://doi.org/10.1016/J.MEMSCI.2005.10.032.

[169] J.M. Hutchinson, Physical aging of polymers, Prog. Polym. Sci. 20 (1995) 703–760, https://doi.org/10.1016/0079-6700(94)00001-I.

[170] R.R. Tiwari, J. Jin, B.D. Freeman, D.R. Paul, Physical aging, CO2 sorption and plasticization in thin films of polymer with intrinsic microporosity (PIM-1), J. Membr. Sci. 537 (2017) 362–371, https://doi.org/10.1016/J.MEMSCI.2017.04.069.

[171] L. Cui, W. Qiu, D.R. Paul, W.J. Koros, Physical aging of 6FDA-based polyimide membranes monitored by gas permeability, Polymer (Guildf.) (2011), https://doi.org/10.1016/j.polymer.2011.05.052.

[172] W.H. Lin, T.S. Chung, Gas permeability, diffusivity, solubility, and aging characteristics of 6FDA-durene polyimide membranes, J. Membr. Sci. (2001), https://doi.org/10.1016/S0376-7388(01)00333-7.

[173] C. Tsvigu, E. Pavesi, M.G. De Angelis, M. Giacinti Baschetti, Effect of relative humidity and temperature on the gas transport properties of 6FDA–6FpDA polyimide: experimental study and modelling, J. Membr. Sci. 485 (2015) 60–68, https://doi.org/10.1016/J.MEMSCI.2015.02.032.

[174] L. Ansaloni, M. Minelli, M. Giacinti Baschetti, G.C. Sarti, Effect of relative humidity and temperature on gas transport in matrimid®: experimental study and modeling, J. Membr. Sci. 471 (2014) 392–401, https://doi.org/10.1016/J.MEMSCI.2014.08.019.

[175] G.Q. Chen, C.A. Scholes, G.G. Qiao, S.E. Kentish, Water vapor permeation in polyimide membranes, J. Membr. Sci. 379 (2011) 479–487, https://doi.org/10.1016/J.MEMSCI.2011.06.023.

[176] R. Casadei, M.G. Baschetti, M.J. Yoo, H.B. Park, L. Giorgini, Pebax® 2533/Graphene oxide nanocomposite membranes for carbon capture, Membranes 10 (2020) 188, https://doi.org/10.3390/MEMBRANES10080188.

[177] M. Minelli, M. Giacinti Baschetti, D.T. Hallinan, N.P. Balsara, Study of gas permeabilities through polystyrene-block-poly(ethylene oxide) copolymers, J. Membr. Sci. 432 (2013) 83–89, https://doi.org/10.1016/J.MEMSCI.2012.12.038.

[178] S.J. Metz, M.H.V. Mulder, M. Wessling, Gas-permeation properties of poly (ethylene oxide) poly(butylene terephthalate) block copolymers, Macromolecules 37 (2004) 4590–4597, https://doi.org/10.1021/MA049847W/ASSET/IMAGES/LARGE/MA049847WF00008.JPEG.

[179] R. Castro-Muñoz, J. González-Valdez, New trends in biopolymer-based membranes for pervaporation, Molecules 24 (2019) 3584, https://doi.org/10.3390/MOLECULES24193584, 2019, Vol. 24, Page 3584.

[180] M.R. Ketabchi, S. Babamohammadi, W.G. Davies, M. Gorbounov, S. Masoudi Soltani, Latest advances and challenges in carbon capture using bio-based sorbents: a state-of-the-art review, Carbon Capture Sci. Technol. 6 (2023) 100087, https://doi.org/10.1016/J.CCST.2022.100087.

[181] A. Jha, A. Kumar, Biobased technologies for the efficient extraction of biopolymers from waste biomass, Bioproc. Biosyst. Eng. 42 (2019) 1893–1901, https://doi.org/10.1007/S00449-019-02199-2/FIGURES/1.

[182] F. Russo, F. Galiano, A. Iulianelli, A. Basile, A. Figoli, Biopolymers for sustainable membranes in CO2 separation: a review, Fuel Process. Technol. 213 (2021) 106643, https://doi.org/10.1016/J.FUPROC.2020.106643.

[183] Michael Niaounakis, Biopolymers: Processing and Products, 2014.

[184] M. Lackner, Bioplastics, Kirk-Othmer Encyclopedia of Chemical Technology, 2015, pp. 1–41, https://doi.org/10.1002/0471238961.KOE00006.

[185] V. Vatanpour, B. Yavuzturk Gul, B. Zeytuncu, S. Korkut, G. İlyasoğlu, T. Turken, M. Badawi, I. Koyuncu, M.R. Saeb, Polysaccharides in fabrication of membranes: a review, Carbohydr. Polym. 281 (2022) 119041, https://doi.org/10.1016/J.CARBPOL.2021.119041.

[186] H.P.S. Abdul Khalil, A.H. Bhat, A.F. Ireana Yusra, Green composites from sustainable cellulose nanofibrils: a review, Carbohydr. Polym. 87 (2012) 963–979, https://doi.org/10.1016/J.CARBPOL.2011.08.078.

[187] Y. Aitomäki, K. Oksman, Reinforcing efficiency of nanocellulose in polymers, React. Funct. Polym. 85 (2014) 151–156, https://doi.org/10.1016/J.REACTFUNCTPOLYM.2014.08.010.

[188] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Cellulose: fascinating biopolymer and sustainable raw material, Angew. Chem. Int. Ed. 44 (2005) 3358–3393, https://doi.org/10.1002/ANIE.200460587.

[189] M. Zhang, T. Xu, Q. Zhao, K. Liu, D. Liang, C. Si, Cellulose-based materials for carbon capture and conversion, Carbon Capture Sci. Technol. 10 (2024) 100157, https://doi.org/10.1016/J.CCST.2023.100157.

[190] K.A. Adegoke, K.O. Oyedotun, J.O. Ighalo, J.F. Amaku, C. Olisah, A.O. Adeola, K.O. Iwuozor, K.G. Akpomie, J. Conradie, Cellulose derivatives and cellulose-metal-organic frameworks for CO2 adsorption and separation, J. CO2 Util. 64 (2022) 102163, https://doi.org/10.1016/J.JCOU.2022.102163.

[191] B. Yavuzturk Gul, E. Pekgenc, V. Vatanpour, I. Koyuncu, A review of cellulose-based derivatives polymers in fabrication of gas separation membranes: recent developments and challenges, Carbohydr. Polym. 321 (2023) 121296, https://doi.org/10.1016/J.CARBPOL.2023.121296.

[192] D. Nikolaeva, K. Verachtert, I. Azcune, J.C. Jansen, I.F.J. Vankelecom, Influence of ionic liquid-like cationic pendants composition in cellulose based polyelectrolytes on membrane-based CO2 separation, Carbohydr. Polym. 255 (2021) 117375, https://doi.org/10.1016/J.CARBPOL.2020.117375.

[193] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B. D. Freeman, Energy-efficient polymeric gas separation membranes for a sustainable future: a review, Polymer (Guildf.) 54 (2013) 4729–4761, https://doi.org/10.1016/J.POLYMER.2013.05.075.

[194] F. Zhang, J. Dou, H. Zhang, Mixed membranes comprising carboxymethyl cellulose (as capping agent and gas barrier matrix) and nanoporous ZIF-L nanosheets for gas separation applications, Polymers 10 (2018) 1340, https://doi.org/10.3390/POLYM10121340, 2018, Vol. 10, Page 1340.

[195] M.S. Rahman, M.S. Hasan, A.S. Nitai, S. Nam, A.K. Karmakar, M.S. Ahsan, M.J. A. Shiddiky, M.B. Ahmed, Recent developments of carboxymethyl cellulose, Polymers 13 (2021) 1345, https://doi.org/10.3390/POLYM13081345/S1.

[196] J. Wang, S.C. Abbas, L. Li, C.C. Walker, Y. Ni, Z. Cai, Cellulose membranes: synthesis and applications for water and gas separation and purification, Membranes 14 (2024) 148, https://doi.org/10.3390/MEMBRANES14070148, 2024, Vol. 14, Page 148.

[197] Z. Bashir, S.S.M. Lock, N.e. Hira, S.U. Ilyas, L.G. Lim, I.S.M. Lock, C.L. Yiin, M. A. Darban, A review on recent advances of cellulose acetate membranes for gas separation, RSC Adv. 14 (2024) 19560–19580, https://doi.org/10.1039/D4RA01315H.

[198] Y. Teramoto, Functional thermoplastic materials from derivatives of cellulose and related structural polysaccharides, Molecules 20 (2015) 5487–5527, https://doi.org/10.3390/MOLECULES20045487, 20 (2015) 5487–5527.

[199] S. Nithin Mithra, S.S. Ahankari, Nanocellulose-based membranes for CO2 separation from biogas through the facilitated transport mechanism: a review, Mater. Today Sustain. 19 (2022) 100191, https://doi.org/10.1016/J.MTSUST.2022.100191.

[200] X. Xu, F. Liu, L. Jiang, J.Y. Zhu, D. Haagenson, D.P. Wiesenborn, Cellulose nanocrystals vs. cellulose nanofibrils: a comparative study on their microstructures and effects as polymer reinforcing agents, ACS Appl. Mater. Interfaces 5 (2013) 2999–3009, https://doi.org/10.1021/AM302624T/ASSET/IMAGES/LARGE/AM-2012-02624T_0017.JPEG.

[201] P. Phanthong, P. Reubroycharoen, X. Hao, G. Xu, A. Abudula, G. Guan, Nanocellulose: extraction and application, Carbon Resour. Conver. 1 (2018) 32–43, https://doi.org/10.1016/J.CRCON.2018.05.004.

[202] A. Dufresne, Nanocellulose: a new ageless bionanomaterial, Mater. Today 16 (2013) 220–227, https://doi.org/10.1016/J.MATTOD.2013.06.004.

[203] M.A. Hubbe, A. Ferrer, P. Tyagi, Y. Yin, C. Salas, L. Pal, O.J. Rojas, Nanocellulose in thin films, coatings, and plies for packaging applications: a review, Bioresources 12 (2017) 2143–2233.

[204] K. Dhali, M. Ghasemlou, F. Daver, P. Cass, B. Adhikari, A review of nanocellulose as a new material towards environmental sustainability, Sci. Total Environ. 775 (2021) 145871, https://doi.org/10.1016/J.SCITOTENV.2021.145871.

[205] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris, Nanocelluloses: a new family of nature-based materials, Angew. Chem. Int. Ed. 50 (2011) 5438–5466, https://doi.org/10.1002/ANIE.201001273.

[206] D. Klemm, E.D. Cranston, D. Fischer, M. Gama, S.A. Kedzior, D. Kralisch, F. Kramer, T. Kondo, T. Lindström, S. Nietzsche, K. Petzold-Welcke, F. Rauchfuß, Nanocellulose as a natural source for groundbreaking applications in materials science: today's state, Mater. Today 21 (2018) 720–748, https://doi.org/10.1016/J.MATTOD.2018.02.001.

[207] D. Klemm, K. Petzold-Welcke, F. Kramer, T. Richter, V. Raddatz, W. Fried, S. Nietzsche, T. Bellmann, D. Fischer, Biotech nanocellulose: a review on progress in product design and today's state of technical and medical applications, Carbohydr. Polym. 254 (2021) 117313, https://doi.org/10.1016/J.CARBPOL.2020.117313.

[208] R. R, E. Philip, D. Thomas, A. Madhavan, R. Sindhu, P. Binod, S. Varjani, M. K. Awasthi, A. Pandey, Bacterial nanocellulose: engineering, production, and applications, Bioengineered 12 (2021) 11463, https://doi.org/10.1080/21655979.2021.2009753.

[209] P.E. Lokhande, P.P. Singh, D.V.N. Vo, D. Kumar, K. Balasubramanian, A. Mubayi, A. Srivastava, A. Sharma, Bacterial nanocellulose: green polymer materials for high performance energy storage applications, J. Environ. Chem. Eng. 10 (2022) 108176, https://doi.org/10.1016/J.JECE.2022.108176.

[210] A.F. Jozala, L.C. de Lencastre-Novaes, A.M. Lopes, V. de Carvalho Santos-Ebinuma, P.G. Mazzola, A. Pessoa-Jr, D. Grotto, M. Gerenutti, M.V. Chaud, Bacterial nanocellulose production and application: a 10-year overview, Appl. Microbiol. Biotechnol. 100 (2016) 2063–2072, https://doi.org/10.1007/S00253-015-7243-4/TABLES/2.

[211] Y. Hosakun, K. Halász, M. Horváth, L. Csóka, V. Djoković, ATR-FTIR study of the interaction of CO2 with bacterial cellulose-based membranes, Chem. Eng. J. 324 (2017) 83–92, https://doi.org/10.1016/J.CEJ.2017.05.029.

[212] S. Kim, E.M.-F. research international, Bioactive compounds from marine processing byproducts–a review, undefined, ElsevierSK Kim, E MendisFood Res. Int. 39 (2006) 383–393, 2006•Elsevier.

[213] D. Xu, S. Hein, K. Wang, Chitosan Membrane in Separation Applications, vol. 24, 2008, pp. 1076–1087, https://doi.org/10.1179/174328408X341762. Https://Doi.Org/10.1179/174328408X341762.

[214] K. Kurita, Chitin and chitosan: functional biopolymers from marine crustaceans, Mar. Biotechnol. 8 (2006) 203–226, https://doi.org/10.1007/S10126-005-0097-5/TABLES/3.

[215] S.Y. Foong, Y.H. Chan, C.L. Yiin, S.S.M. Lock, A.C.M. Loy, J.Y. Lim, P.N.Y. Yek, W. A. Wan Mahari, R.K. Liew, W. Peng, M. Tabatabaei, M. Aghbashlo, S.S. Lam, Sustainable CO2 capture via adsorption by chitosan-based functional biomaterial: a review on recent advances, challenges, and future directions, Renew. Sustain. Energy Rev. 181 (2023) 113342, https://doi.org/10.1016/J.RSER.2023.113342.

[216] N. Hsan, P.K. Dutta, S. Kumar, N. Das, J. Koh, Capture and chemical fixation of carbon dioxide by chitosan grafted multi-walled carbon nanotubes, J. CO2 Util. 41 (2020) 101237, https://doi.org/10.1016/J.JCOU.2020.101237.

[217] S. Kumar, M.Y. Wani, J. Koh, J.M. Gil, A.J.F.N. Sobral, Carbon dioxide adsorption and cycloaddition reaction of epoxides using chitosan–graphene oxide nanocomposite as a catalyst, J. Environ. Sci. 69 (2018) 77–84, https://doi.org/10.1016/J.JES.2017.04.013.

[218] N. Hsan, P.K. Dutta, S. Kumar, R. Bera, N. Das, Chitosan grafted graphene oxide aerogel: synthesis, characterization and carbon dioxide capture study, Int. J. Biol. Macromol. 125 (2019) 300–306, https://doi.org/10.1016/J.IJBIOMAC.2018.12.071.

[219] M. Fan, F. Gai, Y. Cao, Z. Zhao, Y. Ao, Y. Liu, Q. Huo, Structuring ZIF-8-based hybrid material with hierarchical pores by in situ synthesis and thermal treatment for enhancement of CO2 uptake, J. Solid State Chem. 269 (2019) 507–512, https://doi.org/10.1016/J.JSSC.2018.10.027.

[220] E. Luzzi, P. Aprea, M.S. De Luna, D. Caputo, G. Filippone, Mechanically coherent zeolite 13X/chitosan aerogel beads for effective CO2capture, ACS Appl. Mater. Interfaces 13 (2021) 20728–20734, https://doi.org/10.1021/ACSAMI.1C04064/ASSET/IMAGES/LARGE/AM1C04064_0007.JPEG.

[221] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, Macromol. Biosci. 4 (2004) 835–864, https://doi.org/10.1002/MABI.200400043.

[222] B. Gupta, N. Revagade, J. Hilborn, Poly(lactic acid) fiber: an overview, Prog. Polym. Sci. 32 (2007) 455–482, https://doi.org/10.1016/J.PROGPOLYMSCI.2007.01.005.

[223] H.J. Lehermeier, J.R. Dorgan, J.D. Way, Gas permeation properties of poly(lactic acid), J. Membr. Sci. 190 (2001) 243–251, https://doi.org/10.1016/S0376-7388(01)00446-X.

[224] L.T. Lim, R. Auras, M. Rubino, Processing technologies for poly(lactic acid), Prog. Polym. Sci. 33 (2008) 820–852, https://doi.org/10.1016/J.PROGPOLYMSCI.2008.05.004.

[225] F.H. Isikgor, C.R. Becer, Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers, Polym. Chem. 6 (2015) 4497–4559, https://doi.org/10.1039/C5PY00263J.

[226] D. Kun, B. Pukánszky, Polymer/lignin blends: interactions, properties, applications, Eur. Polym. J. 93 (2017) 618–641, https://doi.org/10.1016/J.EURPOLYMJ.2017.04.035.

[227] A. Lisý, A. Ház, R. Nadányi, M. Jablonský, I. Šurina, About hydrophobicity of Lignin: a review of selected chemical methods for lignin valorisation in biopolymer production, Energies 15 (2022), https://doi.org/10.3390/EN15176213.

[228] A. Kumar, Anushree, J. Kumar, T. Bhaskar, Utilization of lignin: a sustainable and eco-friendly approach, J. Energy Inst. 93 (2020) 235–271, https://doi.org/10.1016/J.JOEI.2019.03.005.

[229] G.L.F. Gellerstedt, E.G. Henriksson, Lignins: major sources, structure and properties, monomers, Polym. Comp. Renew. Resour. (2008) 201–224, https://doi.org/10.1016/B978-0-08-045316-3.00009-0.

[230] A. Eraghi Kazzaz, P. Fatehi, Technical lignin and its potential modification routes: a mini-review, Ind. Crops Prod. 154 (2020) 112732, https://doi.org/10.1016/J.INDCROP.2020.112732.

[231] K.M. Hess, J.P. Killgore, W.V. Srubar, Nanoscale hygromechanical behavior of lignin, Cellulose 25 (2018) 6345–6360, https://doi.org/10.1007/S10570-018-2045-3/FIGURES/6.

[232] A.O. Ashogbon, Dual modification of various starches: synthesis, properties and applications, Food Chem. 342 (2021) 128325, https://doi.org/10.1016/J.FOODCHEM.2020.128325.

[233] M. Patil, S.N. Mathad, A.Y. Patil, M.N. Arshad, H.S. Alorfi, M. Puttegowda, A. M. Asiri, A. Khan, N. Azum, Synthesis and characterization of microwave-assisted copolymer membranes of poly(vinyl alcohol)-g-starch-methacrylate and their evaluation for gas transport properties, Polymers 14 (2022) 350, https://doi.org/10.3390/POLYM14020350, 2022, Vol. 14, Page 350.

[234] S. Haouari, D. Rodrigue, A low-cost porous polymer membrane for gas permeation, Materials 15 (2022) 3537, https://doi.org/10.3390/MA15103537.

[235] Y. Qi, H. Wang, K. Wei, Y. Yang, R.Y. Zheng, I.S. Kim, K.Q. Zhang, A review of structure construction of silk fibroin biomaterials from single structures to multi-level structures, Int. J. Mol. Sci. 18 (2017), https://doi.org/10.3390/IJMS18030237.

[236] C. Zhang, D. Song, Q. Lu, X. Hu, D.L. Kaplan, H. Zhu, Flexibility regeneration of silk fibroin in vitro, Biomacromolecules 13 (2012) 2148–2153, https://doi.org/10.1021/BM300541G/ASSET/IMAGES/LARGE/BM-2012-00541G_0002.JPEG.

[237] D.N. Rockwood, R.C. Preda, T. Yücel, X. Wang, M.L. Lovett, D.L. Kaplan, Materials fabrication from Bombyx mori silk fibroin, Nat. Protoc. 6 (2011) 1612–1631, https://doi.org/10.1038/NPROT.2011.379.

[238] B. Prasad, B. Mandal, Graphene-incorporated biopolymeric mixed-matrix membrane for enhanced CO2 separation by regulating the support pore filling, ACS Appl. Mater. Interfaces 10 (2018) 27810–27820, https://doi.org/10.1021/ACSAMI.8B09377/ASSET/IMAGES/LARGE/AM-2018-093775_0006.JPEG.

[239] C. Aulin, M. Gällstedt, T. Lindström, Oxygen and oil barrier properties of microfibrillated cellulose films and coatings, Cellulose 17 (2010) 559–574, https://doi.org/10.1007/S10570-009-9393-Y/TABLES/2.

[240] M. Minelli, M.G. Baschetti, F. Doghieri, M. Ankerfors, T. Lindström, I. Siró, D. Plackett, Investigation of mass transport properties of microfibrillated cellulose (MFC) films, J. Membr. Sci. 358 (2010) 67–75, https://doi.org/10.1016/J.MEMSCI.2010.04.030.

[241] Z. Tong, W.S.W. Ho, Facilitated transport membranes for CO2 separation and capture, Separ. Sci. Technol. 52 (2017) 156–167, https://doi.org/10.1080/01496395.2016.1217885.

[242] T. Merkel, R. Baker, P. Hao, J. Kniep, Z. He, Y. (Ivy, Huang, W. Salim, Carbon capture with membranes: an opportunity revisited, J. Membr. Sci. 738 (2025) 124829, https://doi.org/10.1016/J.MEMSCI.2025.124829.

[243] Y. Yang, Y. Han, C. Zou, R. Pang, J. Hu, K. Chen, W.S.W. Ho, A commercial-size prototype of countercurrent spiral-wound membrane module for flue gas CO2 capture, J. Membr. Sci. 696 (2024) 122520, https://doi.org/10.1016/J.MEMSCI.2024.122520.

[244] T.C. Merkel, M. Zhou, R.W. Baker, Carbon dioxide capture with membranes at an IGCC power plant, J. Membr. Sci. 389 (2012) 441–450, https://doi.org/10.1016/J.MEMSCI.2011.11.012.

[245] Y. Han, W.S.W. Ho, Y. Han, W.S.W. Ho, Moving beyond 90% carbon capture by highly selective membrane processes, Membranes 12 (2022), https://doi.org/10.3390/MEMBRANES12040399, 12 (2022).

[246] C. Clasen, T. Wilhelms, W.M. Kulicke, Formation and characterization of chitosan membranes, Biomacromolecules 7 (2006) 3210–3222, https://doi.org/10.1021/BM060486X.

[247] J. Ge, Y. Cui, Y. Yan, W. Jiang, The effect of structure on pervaporation of chitosan membrane, J. Membr. Sci. 165 (2000) 75–81, https://doi.org/10.1016/S0376-7388(99)00228-8.

[248] M. Pieróg, J.O.-C.-… on C. and, undefined, Thermal degradation of double crosslinked hydrogel chitosan membranes, Bibliotekanauki.Pl. (2012).

[249] D. de Britto, S.P. Campana-Filho, Kinetics of the thermal degradation of chitosan, Thermochim. Acta 465 (2007) 73–82, https://doi.org/10.1016/J.TCA.2007.09.008.

[250] S.Y. Bae, K.H. Lee, S.C. Yi, H.T. Kim, Y.H. Kim, H. Kumazawa, CO2, N2 gas sorption and permeation behavior of chitosan membrane, Kor. J. Chem. Eng. 15 (1998) 223–226, https://doi.org/10.1007/BF02707076/METRICS.

[251] R. Borgohain, U. Pattnaik, B. Prasad, B. Mandal, A review on chitosan-based membranes for sustainable CO2 separation applications: mechanism, issues, and the way forward, Carbohydr. Polym. 267 (2021) 118178, https://doi.org/10.1016/J.CARBPOL.2021.118178.

[252] L.A. El-Azzami, E.A. Grulke, Parametric study of CO 2 fixed carrier facilitated transport through swollen chitosan membranes, Ind. Eng. Chem. Res. 48 (2009) 894–902, https://doi.org/10.1021/ie7016916.

[253] F. Codari, S. Lazzari, M. Soos, G. Storti, M. Morbidelli, D. Moscatelli, Kinetics of the hydrolytic degradation of poly(lactic acid), Polym. Degrad. Stabil. 97 (2012) 2460–2466, https://doi.org/10.1016/J.POLYMDEGRADSTAB.2012.06.026.

[254] F. Galiano, K. Briceño, T. Marino, A. Molino, K.V. Christensen, A. Figoli, Advances in biopolymer-based membrane preparation and applications, J. Membr. Sci. 564 (2018) 562–586, https://doi.org/10.1016/J.MEMSCI.2018.07.059.

[255] C.M.B. Gonçalves, L.C. Tomé, H. Garcia, L. Brandão, A.M. Mendes, I.M. Marrucho, Effect of natural and synthetic antioxidants incorporation on the gas permeation properties of poly(lactic acid) films, J. Food Eng. 116 (2013) 562–571, https://doi.org/10.1016/J.JFOODENG.2012.12.034.

[256] L. Bao, J.R. Dorgan, D. Knauss, S. Hait, N.S. Oliveira, I.M. Maruccho, Gas permeation properties of poly(lactic acid) revisited, J. Membr. Sci. 285 (2006) 166–172, https://doi.org/10.1016/J.MEMSCI.2006.08.021.

[257] R.A. Auras, B. Harte, S. Selke, R. Hernandez, Mechanical, physical, and barrier properties of poly(lactide) films, J. Plastic Film Sheeting 19 (2003) 123–135, https://doi.org/10.1177/8756087903039702.

[258] T. Messin, S. Marais, N. Follain, A. Guinault, V. Gaucher, N. Delpouve, C. Sollogoub, Biodegradable PLA/PBS multinanolayer membrane with enhanced barrier performances, J. Membr. Sci. 598 (2020) 117777, https://doi.org/10.1016/J.MEMSCI.2019.117777.

[259] T. Komatsuka, A. Kusakabe, K.N.- Desalination, Characterization and Gas Transport Properties of Poly (Lactic Acid) Blend Membranes, Elsevier, 2008 undefined 2008.

[260] J.R. Rocca-Smith, N. Chau, D. Champion, C.H. Brachais, E. Marcuzzo, A. Sensidoni, F. Piasente, T. Karbowiak, F. Debeaufort, Effect of the state of water and relative humidity on ageing of PLA films, Food Chem. 236 (2017) 109–119, https://doi.org/10.1016/J.FOODCHEM.2017.02.113.

[261] S. Farah, D.G. Anderson, R. Langer, Physical and mechanical properties of PLA, and their functions in widespread applications — a comprehensive review, Adv. Drug Deliv. Rev. 107 (2016) 367–392, https://doi.org/10.1016/J.ADDR.2016.06.012.

[262] K.D. Cocon, A. Duvieusart, C. Molina-Fernández, Y. Hartanto, P. Luis, Recyclable bio-based polylactic acid gas-liquid membrane contactor for carbon capture process, Carbon Capture Sci. Technol. 15 (2025) 100428, https://doi.org/10.1016/J.CCST.2025.100428.