Chemical and Process Engineering: New Frontiers, 2026, 47(1), e119
DOI: 10.24425/cpe.2026.155557

Reactive modification of PET with 1,5–pentanediol: Polymer properties and porous membrane formation via wet phase inversion

Paulina Rajewska[1,2*], Jolanta Janiszewska[1], Maciej Dębowski[2], Magdalena Mazurek-Budzyńska[2], Dominik Wołosz[2], Paweł Grzegorz Parzuchowski[2]

[1] Łukasiewicz Research Network – Institute for Sustainable Technologies, Pulaskiego 6/10, 26-600 Radom, Poland
[2] Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

*** Corresponding author, e-mail:**
paulina.rajewska@itee.lukasiewicz.gov.pl
paulina.rajewska2@dokt.pw.edu.pl

5th Seminar on Practical Aspects
of Chemical Engineering PAIC 2025,
22–23 September 2025,
Zaniemyśl, Poland.
Guest Editors:
Andżelika Krupińska
and Sylwia Włodarczak.

Article info:
Received: 25 August 2025
Revised: 30 October 2025
Accepted: 02 December 2025

Abstract

Pressure-driven membrane processes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are essential in water treatment, food, pharmaceutical, and wastewater applications. Poly(ethylene terephthalate) (PET) offers high mechanical strength, chemical resistance, and thermal stability, making it a promising alternative to conventional polymers used in membrane preparation. However, its poor solubility in environmentally benign solvents limits its application in wet phase inversion technology. This study proposes a reactive modification of PET via glycolysis with 1,5–pentanediol to enhance solubility in less toxic solvents. The two-step process – PET depolymerisation and subsequent polycondensation – yields poly(pentamethylene terephthalate), characterised by ^{1}H NMR, gel permeation chromatography (GPC) and contact angle measurements. The modification reduces crystallinity, improves chain flexibility, and significantly increases solubility in solvents such as THF, Cyrene®, and DMF at 40 °C. Membranes prepared from Cyrene® solutions via wet phase inversion exhibit a porous, finger-like morphology confirmed by SEM. The hydrophilicity of the modified PET surface increased markedly (contact angle reduction from 110° to 65°). Combining chemical modification with a bio-based solvent provides a practical, sustainable pathway for producing PET-based membranes. The results demonstrate strong potential for developing environmentally friendly, durable membrane materials for advanced separation processes.

Keywords
glycolysis, chemical modification of PET, wet phase inversion process

1. INTRODUCTION

Pressure-driven membrane techniques, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), are among the most critical separation processes used in water and wastewater treatment, as well as the food, biotechnology and pharmaceutical industries (Aziz et al., 2024; Foorginezhad, 2025; García-Ávila et al., 2025). These technologies rely on selective, semi-permeable barriers that separate components based on particle size and physicochemical interactions under applied pressure gradients.

The global membrane filtration market is experiencing rapid growth, with a projected compound annual growth rate (CAGR) of approximately 6–8% between 2023 and 2030 (Meticulous Research, 2023). Key factors driving this growth include increasing water scarcity, rising industrial and municipal wastewater generation, and tightening environmental regulations, as well as the demand for high-quality processed food and beverages (Meticulous Research, 2023). In addition, the shift towards sustainable and decentralized water treatment solutions has positioned membrane technologies as core components of modern purification systems.

Pressure-driven membrane processes are characterised by high separation efficiency, modularity, and relatively low energy consumption compared to traditional separation methods such as distillation or adsorption (Francis et al., 2022). The modular design of membrane systems allows flexible integration into various industrial processes, ranging from large-scale desalination plants to compact bioreactor units. Polymeric and ceramic membranes are primarily used in pressure-driven membrane processes. Polymers such as poly(ethersulfone) (PES), poly(vinylidene fluoride) (PVDF), poly(acrylonitrile) (PAN), cellulose acetate (CA), and polyimide (PI) are widely employed due to their ease of fabrication, moderate cost, and versatility. Nonetheless, despite continuous progress, polymer membranes face several long-standing challenges. These include chemical degradation, thermal instability, and, most notably, fouling – the progressive deposition of colloids, organics, and biological matter on the membrane surface or within its pores (Aziz et al., 2024; Foorginezhad, 2025; García-Ávila et al, 2025; Goh and Ismail, 2018). Fouling not only decreases flux and selectivity but also increases operational costs and energy consumption.

Consequently, recent research has focused on extending membrane lifespan and improving fouling resistance through chemical modification, surface functionalisation, or composite formation. The overarching goal has been to develop membranes that are simultaneously highly permeable, selectively efficient, and resistant to fouling and chemical attack – all while maintaining manufacturability and environmental compatibility.

Over that past decade, substantial progress has been made in designing polymer-based membranes that incorporate inorganic nanomaterials, resulting in mixed-matrix membranes (MMMs) that combine the ease of processing and mechanical flexibility of polymers with the functional advantages of nanofillers (Yang et al., 2020). Nanomaterials, such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), graphene oxide (GO), and metal-organic frameworks (MOFs), have been incorporated to enhance membrane hydrophilicity, antifouling behaviour, and permeability. For example, a recent review (Arundhathi et al., 2024) summarises how embedding nanofillers improves hydrophilicity and fouling resistance across diverse separation applications. Similarly, in MOF-based MMMs used for gas separation, interfacial defects, filler agglomeration, and poor filler-polymer compatibility have been identified as key factors limiting performance (Yu et al., 2024). The in situ generation of Zr-based nanoparticles within a polymer matrix facilities a more uniform nanoparticle dispersion, greater hydrophilicity, and improved antifouling properties, outperforming simple blending approaches (Zhang et al., 2021). Despite substantial advances, issues such as nanoparticle agglomeration, non-selective voids, and long-term stability persist. Addressing these challenges – through improved filler functionalization, in situ growth, enhanced interfaces, and real-world testing – remains essential for the practical progress of MMM (Yang et al., 2020).

Surface modification represents another widely studied route to enhance performance. Plasma treatment, UV grafting, polydopamine, and zwitterionic polymers are among the established techniques for limiting fouling (Goh and Ismail, 2018). However, many such modifications are applied post-fabrication and tend to be unstable under harsh operating conditions or over long periods.

The wet phase inversion method remains the most widely used route for producing asymmetric polymer membranes because the solvent–polymer–nonsolvent interplay controls demixing and, consequently, the skin layer and substructure formed during solidification (Bohr et al., 2023). Solvent properties – especially affinity to polymer and nonsolvent, viscosity, and mass transfer rates – determine demixing type and, ultimately, pore morphology (Hu et al., 2024; Sahu et al., 2024). While polar aprotic solvents such as NMP, DMF and DMAc have historically been preferred, recent work has focused on solvent engineering and substitution with greener alternatives (e.g., Cyrene™, γ-valerolactone, PolarClean) that can reproduce desirable phase-inversion kinetics with lower toxicity and environmental impact (Keirouz et al., 2024; Naziri Mehrabani et al., 2022). Laboratory advances, including co-solvent formulations, additive-assisted phase inversion, and scalable techniques, demonstrate that the interplay between chemistry and process is crucial for producing reproducible, high-quality membranes (Ma et al., 2024).

Grylewicz et al. (2021) demonstrated that solvent choice is a critical determinant of membrane structure, with affinity, viscosity, and exchange rates shaping demixing and resulting microstructure. Moreover, the environmental impact of conventional solvents used in membrane fabrication has become a growing concern. The phase inversion technique – though versatile and widely applied – typically relies on polar aprotic solvents, all of which are linked to significant toxicity and are now regulated under the EU's REACH framework. This regulatory push and environmental focus drive ongoing research into greener, safer solvents, including ionic liquids and DESs with adjustable properties and lower volatility. Parallel efforts aim to develop new polymer–solvent systems that operate efficiently in benign media, thereby reducing both ecological burden and health risks while maintaining key performance parameters.

Within this context, poly(ethylene terephthalate) (PET) – one of the most abundantly produced thermoplastics – has attracted increasing attention as a potential membrane material. Traditionally associated with textiles and beverage packaging, PET combines mechanical strength, stability, and chemical resistance, making it a promising choice for filtration environments (Pulido et al., 2019).

PET's environmental advantages also stand out. As one of the most widely recycled plastics globally, it offers a widespread and low-cost feedstock. Turning PET waste into membranes supports circular economy goals and sustainable materials management, promising both cost and resource savings (Pulido et al., 2019).

Although the exploration of PET for membrane fabrication is still in the early stages, research in this field is expanding rapidly. A recent review (Kirshanov et al., 2022) explicitly covers preparation techniques, including ion-track technology, electrospinning, and non-solvent-induced phase separation (NIPS), applied to PET and copolyesters. The authors emphasise PET‘s mechanical strength, chemical stability, and recyclability, yet highlight that minimal solubility in standard solvents restricts NIPS application unless special systems or pretreatment are used. Chemical modification of PET to improve solubility and functionality represents a promising pathway towards sustainable membrane fabrication. Approaches include copolymerisation, aminolysis, hydrolysis, and glycolysis (Arthanareeswaran et al., 2010). Among these, glycolysis – where PET reacts with diols – is particularly attractive thanks to its commercial maturity.

Controlling glycolysis conditions enables partial depolymerisation and the introduction of functional groups, reducing crystallinity and improving compatibility with polar solvents. This opens the door for PET to participate in benign-phase inversion – potentially under much milder, greener conditions than previously possible.

Despite these advantages, relatively few studies have applied glycolysis in this way. Most research focuses on full monomer recovery or blending with other polymers, rather than using modified PET directly. This gap signals a valuable opportunity for innovation.

In parallel, research explores the combination of glycolysis-derived PET fragments with other polymers to enhance processability and tailor membrane properties (Moncada and Dadmun, 2023; Ragaert et al., 2017). These blends can combine circularity with desirable separation properties. In contrast, mechanical recycling methods, such as extrusion or stretching into films, lack control over the pore structure and tend to deliver lower performance (Al-Sabagh et al., 2016).

Blending PET or rPET with other polymers has improved processability and surface properties, as seen in PET–PVDF and PET–PES blends. However, these still often require toxic solvents. Surface modification techniques have shown promise for wettability and fouling reduction (Shakayeva et al., 2024).

Therefore, combining chemical recycling – especially glycolysis – with advanced membrane-forming techniques, like electrospinning or phase inversion, presents a promising strategy for high-performance, eco-conscious membranes (Hassan et al., 2025; Moncada and Dadmun, 2023).

Electrospinning approaches upcycle PET waste into nanofibrous membranes for applications such as oil–water separation, often outperforming conventional polymers. Yet, most techniques use aggressive and toxic solvents. A key limitation for PET membrane technology remains the lack of benign solvent systems compatible with phase inversion. Overcoming this is critical to PET's mainstream use.

Using PET as a raw material for producing filtration membranes represents an innovative approach, which could significantly impact the availability of more efficient and eco-friendly membrane materials. One of the main challenges associated with the use of PET for filtration membranes is its limited solubility in standard solvents, which poses a barrier to the production of membranes by the wet phase inversion method. PET dissolves only in a few powerful and toxic solvents, such as the mixture of trifluoroacetic acid and dichloromethane (TFA/DCM) or chloroform (Karim et al., 2022; Schlüter et al., 2024). These substances are hazardous to both health and the environment, significantly hindering the industrial use of PET in this technology. Therefore, chemical modification of PET to improve its solubility and the search for alternative, less toxic solvents are crucial for developing this technology. Such modifications may include introducing functional groups that change the chemical nature of PET, reducing its crystallinity, and enhancing its solubility in more environmentally friendly solvents (Arthanareeswaran et al., 2010). This solution could pave the way for the production of PET membranes using the wet phase inversion method, which is one of the most commonly used methods for forming porous membrane structures.

In light of the challenges associated with PET processability and solvent limitations, this work proposes a new chemical route for developing sustainable PET-based membranes. Through reactive glycolysis with 1,5–pentanediol followed by polycondensation, poly(pentamethylene terephthalate) is obtained, exhibiting markedly improved solubility and processability. Notably, the modified polymer can be fully dissolved in the bio-based solvent Cyrene® at mild temperatures, offering a non-toxic alternative to conventional solvent systems. Building upon this advancement, the study demonstrates the fabrication of porous membranes by wet phase inversion, thereby overcoming the key limitation of pristine PET. The integration of chemical recycling, green solvent use, and membrane formation within a single framework provides a unified and environmentally responsible approach to PET valorisation. This strategy lays the groundwork for future developments in sustainable polymeric membranes for advanced separation applications.

2. EXPERIMENTAL

2.1. Method of PET modification with 1.5-pentanediol

PET modification is based on the glycolysis process, carried out in two main stages: PET depolymerisation, which involves the breaking of ester bonds in the presence of selected diols, and polycondensation, which allows for the reconstruction of the polymer structure with new functional substituents (Karayannidis et al., 2006; Moncada and Dadmun, 2023). The process was carried out at 180–250 °C, using 96 g of PET (NeoPET 80; NeoGroup) and 52 g of 1,5–pentanediol (synthesis grade, Merck Poland) as the modifier. The reaction was carried out in the presence of an inert gas to prevent degradation of the substrates and final products and the formation of reaction by-products. Zinc(II) acetylacetonate (0.24 g) (purity $> 96\%$; TCI Japan) was used as the catalyst in the reaction, and ethylene glycol was azeotropically distilled during the process in the presence of xylene (reagent grade, Merck Germany). Polycondensation was carried out under reduced pressure (0.05 mbar) at 180 °C, which additionally allowed for the removal of low-molecular-weight fractions and ensured proper control over the structure of the resulting polymer.

2.2. Studies on the physicochemical properties of modified PET

After preparation, the modified PET was subjected to physicochemical studies, including structural analysis using Nuclear Magnetic Resonance Spectroscopy ^{1}H NMR. Samples (15 mg of polymer) were dissolved in 1 mL of solvent: deuterated chloroform ($CDCl_3$). ^{1}H spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard at 20 °C.

The molecular weights (Mn – number average molecular weight, Mw – weight average molecular weight, Mz – average molecular weight and Đindex) of the modified PET were determined by Gel Permeation Chromatography (GPC) using a Malvern Viscotek GPCMax TDA 305 chromatograph, equipped with Jordi Labs DVD Mixed Bed column with 30 cm length and an internal diameter of 7.8 mm. The measuring instrument had four detectors: refractometric, light dispersion, viscometric, and UV-PDA (UV-Photodiode Array) detector. The measurements were conducted at 30 °C with an eluent (DCM) flow rate of 1 mL/min. Polystyrene standard was used as a molecular weight reference. 3 mg of the examined polymer was dissolved in 1.5 mL of a solution containing 99.5% (v/v) DCM and 0.5% (v/v) $CHCl_3$. The prepared sample was vortexed for 24 hours and then filtered through a 0.20 μm syringe filter into a 1.5 mL glass vial.

Structural studies of modified poly(ethylene terephthalate) were performed using the Fourier Transform Infrared Spectroscopy (FT-IR) (BIORADFTS-165 spectrometer). The selected wavenumber range was 4000-400 cm^{-1}, and the resolution was set at 2 cm^{-1} using 16 sample scans.

Furthermore, solubility studies of the resulting modified PET were conducted in selected solvents, such as tetrahydrofuran (THF), Cyrene®, dimethylformamide (DMF), butanol, acetone, and ethyl acetate, at temperatures of 40 °C and 60 °C. The tests were conducted in a climatic chamber at a stirring speed of 300 rpm.

2.3. Membrane preparation and characterisation

Membranes were prepared from the homogeneous solutions using the wet phase inversion process (Fig. 1). Solutions containing 15% of the polymer in the solvent were prepared by heating the mixture at 40 °C or 60 °C (Tab. 1) and a speed of 300 rpm. Then, the homogenous solutions were cast onto a glass plate and immediately immersed in a coagulation bath (deionised water). After the inversion process, membranes were washed with fresh deionised water and stored in a climatic chamber.

The morphology of the produced porous materials was analysed using a Helios 5 PFIB CXe scanning electron microscope (Thermo Fisher Scientific, Inc.) equipped with an Elstar high-resolution field emission SEM column and a Phoenix ion column with inductively coupled Xe+ plasma, as well as a set of Elstar detectors for electron imaging, including an Everhart-Thornley (ETD) secondary electron detector. A working distance of about 4.0 mm and an electron beam acceleration voltage of 5 kV were applied. Before the measurements, all samples were attached to the SEM specimen mounts with an electron conductive Cu tape and sputtered with a 10 nm thick Au layer using a CCU-010 high-vacuum sputtering unit (Safematic GmbH).

Surface porosity analysis was carried out on images obtained using a scanning electron microscope (SEM, Helios PFIB, Thermo Fisher Scientific) at a magnification of 10 000×, an accelerating voltage of 5 kV, and a beam current of 0.10 nA. Digital image processing (*ImageJ*, Software) was performed on the obtained micrographs to determine the fraction of the pore area relative to the total analysed surface area.

SEM images were imported in RGB format and converted to grayscale. To enhance the contrast between the pores and the solid material, linear normalisation of the intensity histogram was applied (rescaling within the 2–98 percentile range).

Binary segmentation was performed using Otsu's automatic thresholding method, which allowed for the separation of bright areas corresponding to the solid phase from dark areas representing pores. Pixels with intensity values below the threshold were classified as pores. Subsequently, morpholog-

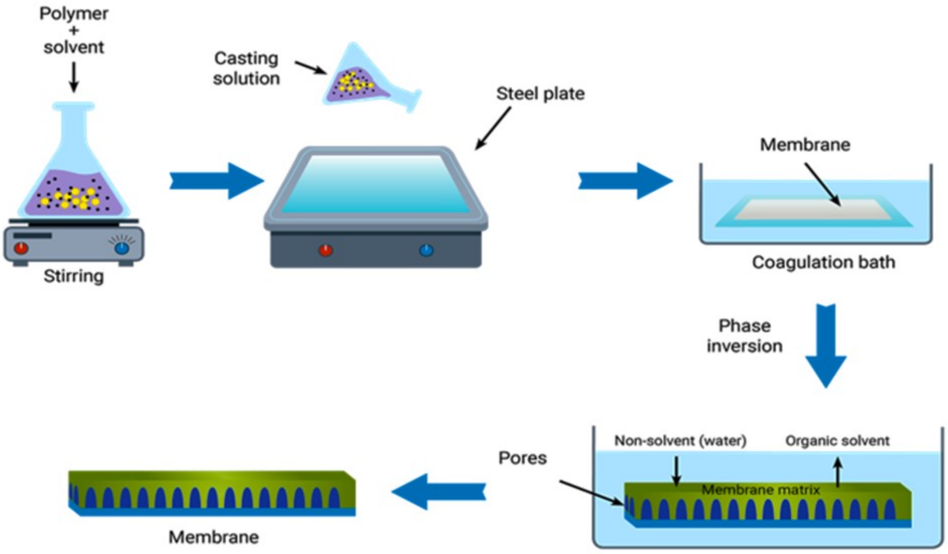


Figure 1. Scheme of the production of porous materials by the wet phase inversion process.

ical operations were applied to improve the continuity of the pore boundaries, including the removal of small objects (< 80 pixels), filling of small holes (< 150 pixels), and morphological closing with a structural element of radius 2 pixels.

Based on the resulting binary mask, the number of pixels corresponding to pores (N_p) and the total number of pixels in the analysed image (N_i) were determined. Given the horizontal field width (HFW = 41.4 µm) and the image resolution (1078 pixels), the linear pixel size was calculated as:

$$s = \frac{\text{HFW}}{N_x} \tag{1}$$

and the area of a single pixel as:

$$A_{px} = s^2 \tag{2}$$

The total image area was then determined as:

$$A_{\text{tot}} = N_t \cdot A_{px} \tag{3}$$

and the total pore area as:

$$A_{\text{pore}} = N_p \cdot A_{px} \tag{4}$$

Surface porosity (P_s) was defined as the ratio of the total pore area to the total analyzed area, expressed as a percentage:

$$P_s = \frac{A_{\text{pore}}}{A_{\text{tot}}} \cdot 100\% \tag{5}$$

The contact angles of polymer surfaces were measured using the sessile drop method (goniometer) (Fig. 2). A special measurement setup was used, consisting of a microscope, a camera, and a computer with an installed digital image acquisition and processing system. The wettability of the polymer surfaces was determined using a goniometer.

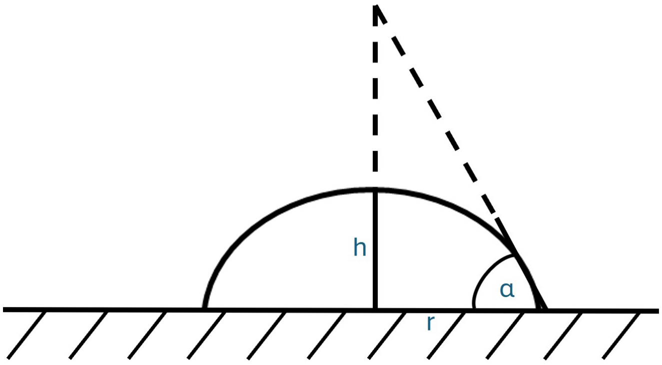


Figure 2. A drop of liquid on a solid surface in the presence of air.

The value of the contact angle was calculated by the formula (Sulek and Wasilewski, 2006):

$$\tan\alpha = \frac{2hr}{r^2 - h^2} \tag{6}$$

where: r – droplet radius, h – droplet height. The measurement result was the average value from five independent measurement series.

The water uptake of the membranes was evaluated gravimetrically using a standard swelling test based on the following protocol: Membrane samples were dried to constant weight at 60 °C. The dry mass was recorded as W_d. Dried membrane samples were completely immersed in distilled water at room temperature for 24 hours to allow for equilibrium swelling. After the immersion period, samples were removed and gently blotted with filter paper to eliminate excess surface water without damaging the membrane. The mass of the swollen (hydrated) membrane was immediately measured and recorded as W_w. The water uptake (swelling degree) was calculated using the Eq. (7) (Ndlwana et al., 2020).

$$\text{Water uptake}\,(\%) = \frac{W_w - W_d}{W_d} \cdot 100\% \tag{7}$$

3. RESULTS

Modification of PET with pentanediol leads to the formation of poly(pentamethylene terephthalate) (Fig. 3). The reaction of PET with 1,5–pentanediol is not stoichiometric. This means that some repeating units containing fragments derived from ethylene glycol remain in the structure (both at the ends of the PET chain and in the middle). By introducing longer diol chains into PET, the stiffness of the polymer and the degree of its crystallinity are reduced, while its flexibility is improved (Karayannidis et al., 2006; Moncada and Dadmun, 2023).

The use of Gel Permeation Chromatography (GPC) in the analysis of the synthesised poly(pentamethylene terephthalate) allowed the determination of parameters related to molecular weight, such as average molecular weights and polydispersity index.

The *Mn* (16 150 [Da]) value reflects the average molecular weight, calculated as the ratio of the total mass of the particles to their number, indicating the presence of smaller particles in the mixture. A higher *Mw* (33 792 [Da]) value suggests the presence of heavier particles, which have a greater impact on the weight average. A high *Mz* (53 095 [Da]) value confirms the presence of particles with a very high molar mass. Additionally, a polydispersity index (*Đ*) of approximately 2.5 indicates a moderately broad molecular weight distribution. This broad molecular weight distribution may be due to the synthetic process, favouring the formation of both low- and high-molecular-weight fractions. Large particles can positively affect the material's mechanical properties, but increased polydispersity can reduce suitability for further processing. Similar values and relationships have also been described in the literature (Lu et al., 2017), including for biodegradable copolyesters based on 1.5-pentanediol, where the *Đ index* was also in the range of 2–2.5, confirming that this is a characteristic feature of this type of material.

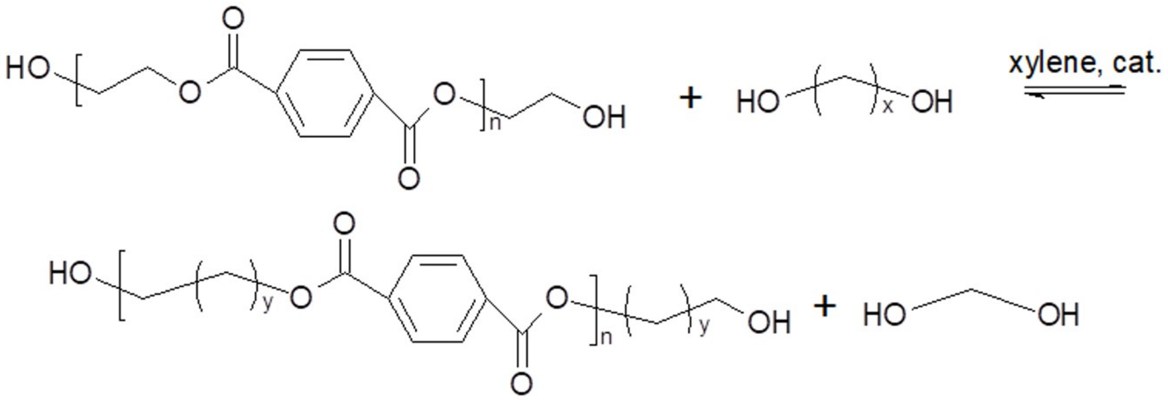


Figure 3. Synthesis reaction of poly(pentanediol terephthalate); $x = 5$; $y = 4$.

FT-IR analyses were performed to confirm the modification of the PET chain. The FT-IR spectrum (Fig. 4) for PET modification with 1,5–pentanediol shows characteristic absorption bands that can be assigned to specific functional groups in the sample:

- Around 2850–2950 cm^{-1}: Peaks in this region suggest C–H stretching from the $–CH_2–$ groups;
- Around 1460–1470 cm^{-1} and 1375 cm^{-1}: These peaks indicate bending vibrations of $–CH_2–$ and $–CH_3$;
- Around 1050–1150 cm^{-1}: Strong absorption in this region can be attributed to C–O stretching, characteristic of alcohols;
- Below 1000 cm^{-1}: Peaks in this region are often caused by different bending modes and vibrations of the fingerprint region.

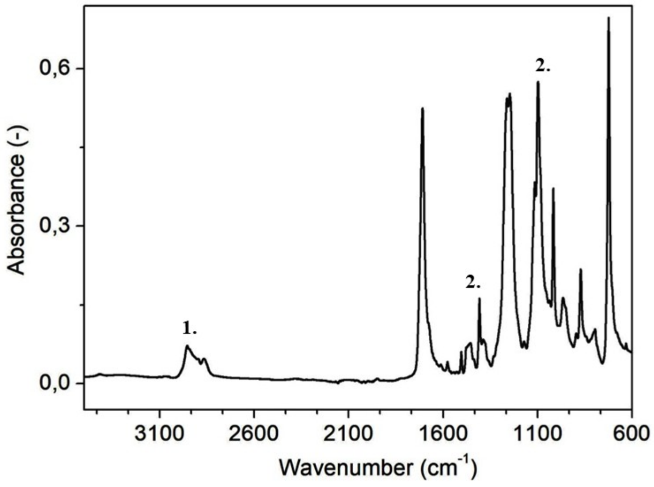


Figure 4. FT-IR spectra: PET modification with 1,5–pentanediol.

Taking this into account, key peaks confirming the structure include:

- (1.) C–H stretching around 2850–3000 cm^{-1};
- (2.) C–O stretching around 1050–1150 cm^{-1}.

C–H stretching and bending vibrations around 2850–3000 cm^{-1} and 1460–1470 cm^{-1} confirm the alkane structure. Strong absorption around 1050–1150 cm^{-1} confirms the presence of C–O bonds.

The efficiency of the glycolysis reaction of poly(ethylene terephthalate) and 1,5–pentanediol was monitored by examining the structure of the obtained material using ^1H NMR (Fig. 5).

Deuterated chloroform ($CDCl_3$) was used as the solvent to record the spectrum and chemical shift values (δ) are given in ppm relative to an internal standard ($CHCl_3$ signal at 7.26 ppm). The following characteristic signals were recorded in Table 1.

Similar chemical shift ranges have been described in the literature for PET glycolysis products using aliphatic diols, including 1,4-butanediol and 1,6-hexanediol, where shifts of the methyl and hydroxyalkyl groups were observed in the range of 1.2–2.2 ppm, and signals of the ester $–CH_2–O–$ groups in the range of 3.9–4.4 ppm were observed (Moncada and Dadmun, 2023; Chemicalbook).

Analysis of the ^1H NMR spectrum confirmed the glycolysis reaction of PET. An aromatic signal at 8.08 ppm suggests the retention of the terephthalic backbone, characteristic of PET. At the same time, the appearance of numerous signals in the aliphatic range (1.2–2.0 ppm and 3.6–4.4 ppm) indicates the adequate substitution of ethylene residues by 1,5–pentanediol fragments. The presence of characteristic signals for all key pieces of the polymer structure suggests high product purity and the effectiveness of the modification process. Compared to the ^1H NMR spectrum of commercial PET (Tanaka et al., 2016), which contains only signals from aromatic protons (approximately 8.1 ppm) and $–CH_2–O–$ groups in the range of 4.6–4.8 ppm, the analysed product exhibits additional signals from the diol, confirming the occurrence of structural modification. The obtained material can be classified as a glycolysed oligomer with a mixed ester-alcohol structure, representing a potential raw material for membrane production.

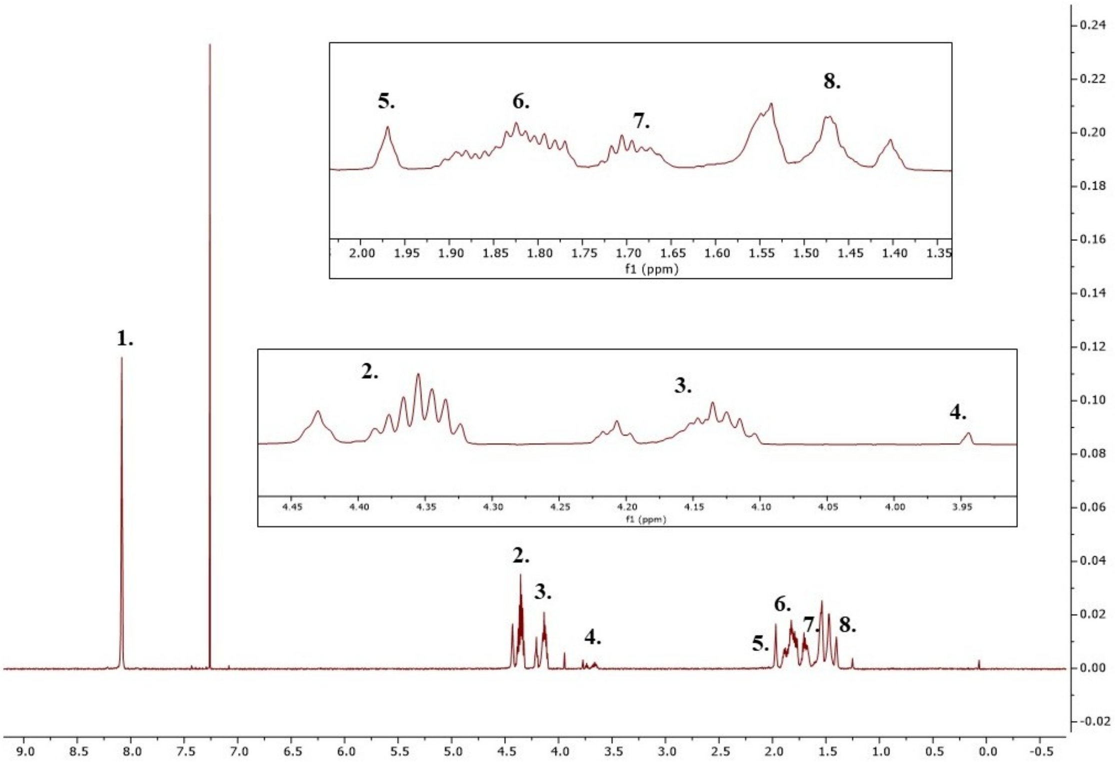


Figure 5. ^{1}H NMR spectrum of the synthesised poly(pentamethylene terephthalate).

Table 1. ^{1}HNMR Spectrum analysis.

Peak No.	[ppm]	Signal type	Chemical group	Signal interpretation
1.	8.07	singlet	–CH aromatic (terephthalate ring of PET)	Aromatic protons of PET (para-substituted ring), confirming retention of PET unit after glycolysis.
2.	4.10–4.43	multiplet	–CH$_2$–O– (ester groups in PET and diol fragments)	–OCH$_2$– protons of PET as well as fragments from 1,5–pentanediol, confirming alcohol exchange in the polymer structure.
3.	3.95–3.63	triplet/ multiplet	terminal –CH$_2$OH (oligomer ends)	–CH$_2$– protons adjacent to –OH or ester, indicating chain ends with free hydroxyls from unreacted or partially reacted diol.
4.	3.95	singlet/ triplet/ multiplet	–CH$_2$ (close to chain end, minor components or artifacts)	Minor/terminal chain signals, of low intensity, likely indicate trace impurities or chain ends.
5.	1.95–2.0	multiplet	–CH$_2$– (next to carbonyl/ester in 1,5–pentanediol)	Methylene protons near a carbonyl or ester group in the diol, within the chain backbone
6.	1.80–1.70	multiplet	–CH$_2$– (internal groups of 1,5–pentanediol)	Methylene protons of pentanediol skeleton, multiplet due to coupling with neighboring CH$_2$ groups.
7.	1.65–1.55	multiplet/ triplet	–CH$_2$– (mid/near-end diol segments)	Coupled methylene protons at the chain end of diol, possible triplet structure .
8.	1.55–1.35	multiplet	–CH$_2$– (end groups of diol, possible minor impurities)	Terminal methylene groups of the diol, or other aliphatic chain segments, multiplet from coupling.

Table 2 presents the effect of PET modification with pentanediol on the solubility of the material in selected solvents at temperatures of 40 °C and 60 °C. The tested poly(pentamethylene terephthalate), obtained by glycolysis of PET with 1,5–pentanediol, exhibited varying solubility depending on the solvent used (Table 2). The material was completely dissolved in tetrahydrofuran (THF), Cyrene®, and dimethylformamide (DMF) at temperatures as low as 40 °C. This behaviour suggests good chemical compatibility of these solvents with the material, resulting from their appropriate polarity and ability to weaken interchain interactions effectively. This facilitates the mobility of the polymer segments and leads to complete dissolution.

Table 2. Solubility of (poly(pentanediol terephthalate)) (samples P2-P7, P91 and pure PET) in selected solvents at 40 °C and 60 °C.

Sample	Solvent	40 °C	60 °C
P2.	THF	Soluble	Soluble
P3.	Butanol	Insoluble	Insoluble
P4.	Acetone	Partially soluble	Partially soluble
P5.	Cyrene®	Soluble	Soluble
P6.	DMF	Soluble	Soluble
P7.	Ethyl acetate	Partially soluble	Partially soluble
P91.	DMSO	Insoluble	Insoluble
PET (pure)	THF, butanol, acetone, Cyrene®, DMF, ethyl acetate	Insoluble	Insoluble

Partial solubility in acetone and ethyl acetate indicates weaker interactions between these solvents and the polymer structure. This may be related to the limited ability of these solvents to interact with the aromatic and stiffer terephthalate segments present in the poly(pentamethylene terephthalate) structure. The aliphatic chains introduced by 1,5–pentanediol provide the material with greater flexibility, but not all solvents can effectively disrupt residual interchain interactions. It is also worth noting that commercial (pure) PET did not dissolve in any of the solvents tested. This phenomenon can be explained by the high degree of crystallinity and the compact structure of PET, which effectively limits the penetration of solvent molecules and prevents the disruption of the ordered network of interchain interactions. The temperature increase to 60 °C was insufficient to disrupt these strong interactions, confirming the high resistance of PET to dissolution processes under standard laboratory conditions (Di Lorenzo, 2024; Karim et al., 2022; Schlüter et al., 2024).

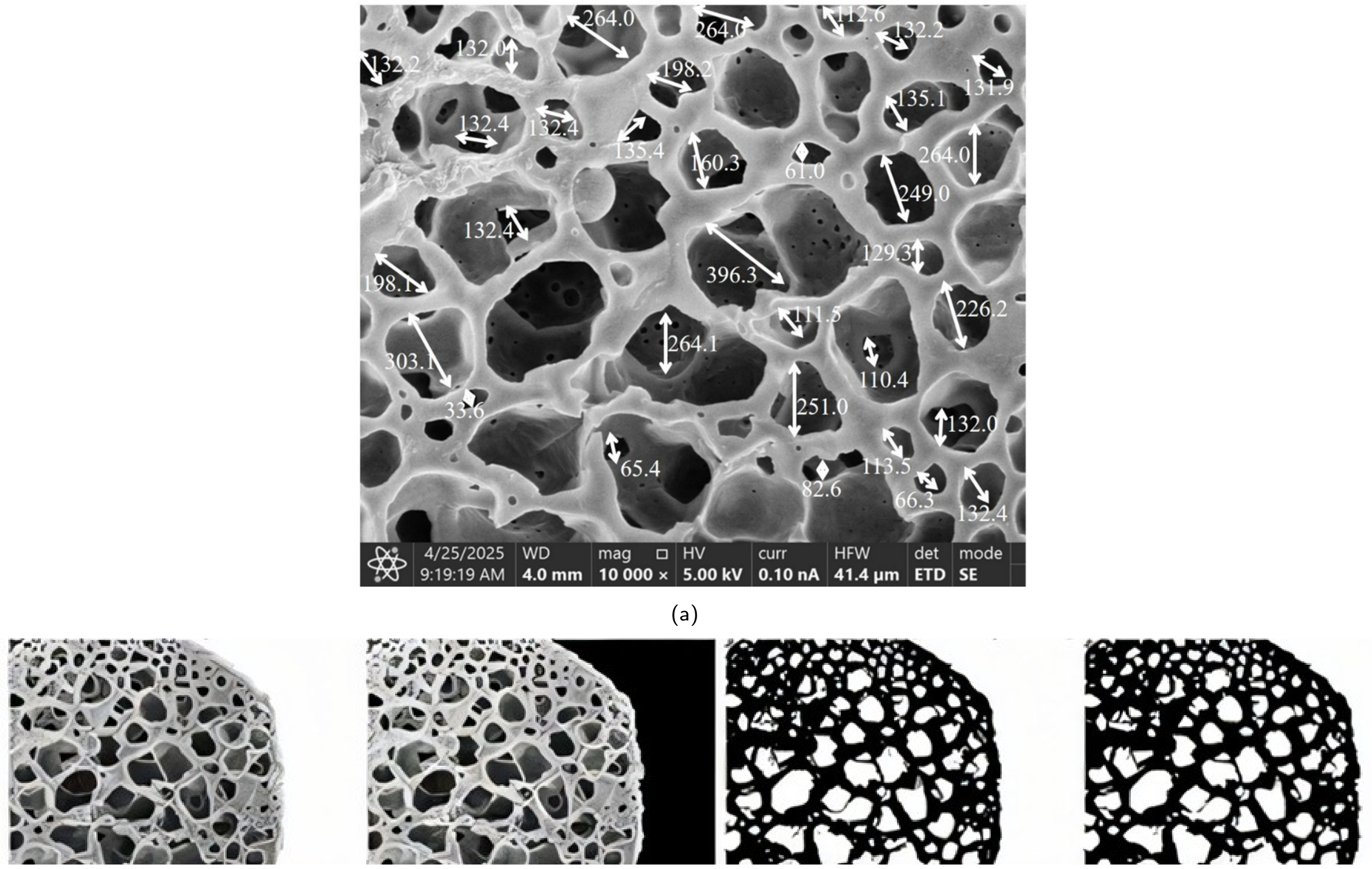
SEM analysis of a cross-sectional membrane produced by phase inversion in a water bath using poly(pentamethylene terephthalate) dissolved in Cyrene® confirms the presence of a porous structure characteristic of membranes obtained by this technique (Figs. 6 and 7).

SEM images revealed a porous membrane surface, which is typical for membranes formed by the phase inversion method (Fig. 6a). The presence of pores in the resulting membrane structure can be attributed to the dynamic exchange between the solvent (Cyrene®) and the antisolvent (water) during the coagulation process. Cyrene® is a highly polar solvent with good miscibility with water and is also characterised by a high ability to rapidly penetrate the coagulation phase (Milescu et al., 2019). Rapid mass transfer leads to the immediate displacement of solvent from the polymer solution and the simultaneous inflow of water into the system. Such rapid phase separation favours the formation of an unstable two-phase system, in which local concentration differences lead to separation into a polymer-rich continuous phase and a solvent phase, which forms closed or open pores (Hu et al., 2024).

Figure 7 shows a cross-sectional photograph of the membrane obtained by the phase inversion method. It is visible that the membrane has a porous, multilayer structure resulting from the rapid exchange of the solvent (Cyrene®) with water. Large, irregular macropores extending through the membrane indicate intensive mixing of the solvent and non-solvent during coagulation. The pores have a distinctly conical, tunnel-like shape, characteristic of membranes with a so-called finger-like structure (Ali et al., 2023; Bohr et al., 2023).

The pore size appears to be quite variable, which may be due to rapid coagulation resulting from the very good miscibility with water of the solvent used, i.e. Cyrene, which in this case behaves as NMP or DMF (Milescu et al., 2019). SEM microscopic analysis combined with digital image processing determined the surface porosity of the poly(pentamethylene terephthalate) filtration membrane to be 39.55%. The range of surface pore diameters, spanning from approximately 60 to 390 nm (Fig. 6a), clearly places the tested membrane in the group of micro- and mesoporous materials, confirming its potential use in microfiltration or low-pressure ultrafiltration processes.

SEM images obtained at 10 000× magnification (Fig. 6a) revealed a well-developed, differentiated surface topography with numerous open pores of irregular shapes. The use of Otsu segmentation and morphological image refinement enabled precise differentiation of porous regions and the polymer phase (Fig. 6b), making the obtained result representative of the actual microstructure of the membrane surface. The literature describes membranes obtained from recycled PET that also exhibit a porous structure after using the phase inversion method. Membranes prepared from waste PET bottles exhibit an asymmetric structure with a macroporous cross-section and a smooth active layer on the surface (Pulido et al., 2019). However, the porosity and morphology of these



(a)

(b)

Figure 6. SEM image of the membrane surface produced by the wet phase inversion method from 1,5–pentanediol-modified PET (a); Successive stages of SEM image processing for surface porosity evaluation: (1) original image, (2) contrast normalisation, (3) Otsu segmentation, (4) final pore mask after morphological corrections (b)

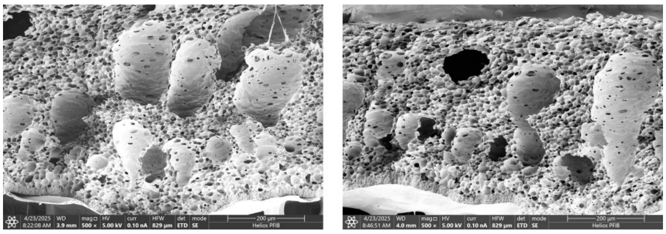


Figure 7. SEM images of cross-sections of a membrane (×500) produced by wet phase inversion from 1,5–pentanediol-modified PET.

membranes can vary depending on the introduced modifiers and process conditions. Studies by (Pulido et al., 2019) show that membranes from PET recyclates struggle to achieve a highly porous structure without adding porophores or intensive mixing while preparing a homogeneous membrane-forming solution, even after modification with plasticisers. Modification of PET with 1,5–pentanediol leads to a reduction in the polymer's crystallinity, thus increasing the mobility of its chain segments. More flexible chains promote dynamic reorganisation during the membrane formation process. Combined with using a highly polar solvent, such as Cyrene®, which effectively dissolves the modified material and mixes intensively with water during coagulation, conditions that favour the formation of a porous morphology are achieved. The tunnel structure observed in SEM images (Fig. 7) results from rapid phase separation initiated by intense mass transfer between Cyrene® and water. Increased chain flexibility may also support this morphology, facilitating material reorganisation during coagulation. This results in membranes with more uniform and controlled porosity, which is crucial for their filtration and mechanical properties.

The contact angle is a valuable indicator of the hydrophobicity or hydrophilicity of a surface; lower values correspond to a greater affinity for water and indicate a more hydrophilic material. Analysis of contact angles using the sessile drop method showed that modification of PET with 1,5–pentanediol significantly affects its surface properties. Commercial PET (110°) exhibits a distinct hydrophobic character resulting from its ordered crystalline structure and rigid, aromatic chemical skeleton (containing benzene rings). PET modified with 1,5–pentanediol becomes more hydrophilic, as reflected by a significant reduction in the contact angle to 65°. This reduced contact angle results from, among other things:

- Disruption of the PET crystalline structure – The introduction of 1,5–pentanediol segments into PET disrupts the regularity of the chain, inhibiting crystallisation and increasing the amorphous phase. This less ordered amorphous structure is characterised by weaker overall intermolecular cohesion and, crucially, significantly better accessibility of polar functional groups to water molecules, which promotes water hydration by the polymer;
- Increased chain flexibility – segments derived from 1,5–pentanediol, thanks to their longer aliphatic –$(CH_2)5$– chains, may contribute to an increase in the overall flexibility of the polymer chain. Compared to stiffer structural elements, such as aromatic rings in polyethylene terephthalate, or shorter aliphatic segments, longer pentamethylene units allow for greater conformational freedom. For example, polymers containing pentamethylene units, such as poly(pentamethylene furoate) (PPeF), exhibit elastomeric properties, characterised by a low elastic modulus (e.g., $E = 9$ MPa for PPeF) and very high elongation at break (over 1000% for PPeF) (Guidotti et al., 2024).

Such increased mobility of polymer chain segments may facilitate dynamic reorganisation of its surface, including the orientation of polar groups. Polymer molecules on the surface can undergo conformational changes upon contact with polar liquids, such as water, which promotes more effective interactions. Similar effects were observed when PET was modified with other diols: Sun et al. (2020) demonstrated that PET modification with, among others, PEG increased the hydrophilicity of the polymers, which translated into better wettability of the resulting material.

The water uptake test was conducted for two types of membranes: a membrane fabricated from PET modified with 1,5–pentanediol and, for comparison, a commercial poly(ethersulfone) microfiltration membrane (PES, MF, TriSep Membrane Filters, Sterlitech). Three separate membrane fragments from each type were tested to ensure reproducibility of the results.

Analysis of the swelling degree of the membranes revealed that both the commercial PES membrane and the membrane prepared from poly(pentamethylene terephthalate) exhibited a low degree of swelling, 1.51% and 1.77%, respectively. Such a small dimensional change indicates that both materials are characterised by a relatively stable polymer matrix, showing limited capacity for water absorption and minimal volumetric expansion in an aqueous environment (Geens et al., 2004). The low swelling level is consistent with the moderate hydrophilicity of the membranes, as evidenced by the contact angle values of approximately 65°, which suggest partial but not complete wettability of the surface.

The limited swelling is a result of the combined effect of the material's chemical structure and the morphology formed during the coagulation process. Although modification of PET with 1,5–pentanediol introduces aliphatic segments that reduce crystallinity and increase chain flexibility, the overall polymer backbone still contains rigid terephthalate units, which limit excessive water absorption. As a consequence, water can easily penetrate and fill the membrane pores, but does not significantly diffuse into the polymer phase, which prevents considerable structural expansion. A similar trend was observed for the commercial PES membrane, which also exhibits moderate hydrophilicity and a porous morphology typical of membranes obtained by phase inversion (Geens et al., 2004; Olivares Moreno and Altintas, 2022). PES possesses aromatic structural fragments that impart mechanical rigidity and dimensional stability in contact with water. The comparable degree of swelling for both membranes thus reflects the dominance of structural and morphological factors – particularly the presence of a continuous, compact polymer framework with limited interaction sites for water molecules – over purely chemical composition. The porous, asymmetric morphology obtained via wet phase inversion further supports this dimensional stability, ensuring that water interacts mainly with the pore system rather than with the polymer bulk.

4. CONCLUSIONS

This paper presents an innovative approach to fabricating filtration membranes based on poly(ethylene terephthalate) (PET), a material known for its high strength and chemical resistance. Although PET has potential for membrane applications, its low solubility in safe solvents limits its practical use in wet phase inversion. Chemical modification of PET by glycolysis with 1,5–pentanediol was proposed to address this issue. The process involved depolymerising PET and repolycondensation, forming a modified copolymer – poly(pentamethylene terephthalate). Modification of PET with 1,5–pentanediol is an effective method for improving its solubility in environmentally friendly solvents and simultaneously enables the production of porous membranes by wet phase inversion. The resulting material demonstrates promising properties for membrane applications, and the use of Cyrene® as a solvent further enhances the environmental impact of this technology. In the context of filtration applications, the obtained morphological parameters and hydrophysical properties indicate that the developed membrane may be an attractive alternative to, for example, commercial PES membranes, offering comparable dimensional stability. The development of such technologies could significantly impact the availability of more sustainable, efficient, and chemically resistant membrane materials in the future.

ACKNOWLEDGEMENTS

This research was financed by the Ministry of Science and Higher Education of Poland under the 2025 subvention for Łukasiewicz Research Network – Institute for Sustainable Technologies (DIR-WNO.705.3.8.2025.A).

REFERENCES

Ali B.T.I., Kusumawati Y., Jaafar J., Sulistiono D.O., Widiastuti N., 2023. Low-cost membrane from polyethylene terephthalate bottle waste for water purification and chromium removal: modification and application. *RSC Adv.*, 13, 8985–8995. DOI: 10.1039/D3RA00827D.

Al-Sabagh A.M., Yehia F.Z., G. Eshaq, Rabie A.M., El-Metwally A.E., 2016. Greener routes for recycling of polyethylene terephthalate. *Egypt. J. Pet.*, 25, 53–64. DOI: 10.1016/j.ejpe.2015.03.001.

Arthanareeswaran G., Mohan D., Raajenthiren M., 2010. Preparation, characterization and performance studies of ultrafiltration membranes with polymeric additive. *J. Membr. Sci.*, 350, 130–138. DOI: 10.1016/j.memsci.2009.12.020.

Arundhathi B., Pabba M., Raj S.S., Sahu N., Sridhar S., 2024. Advancements in mixed-matrix membranes for various separation applications: state of the art and future prospects. *Membranes*, 14, 224. DOI: 10.3390/membranes14110224.

Aziz S., Mazhar A.R., Ubaid A., Shah S.M.H., Riaz Y., Talha T., Jung D.-W., 2024. A comprehensive review of membrane-based water filtration techniques. *Appl. Water. Sci.*, 14, 169. DOI: 10.1007/s13201-024-02226-y.

Bohr S.J., Fei Wang, Metze M., Vukušić J.L., Sapalidis A., Ulbricht M., Nestler B., Barbe S., 2023. State-of-the-art review of porous polymer membrane formation characterization – how numerical and experimental approaches dovetail to drive innovation. *Front. Sustainability*, 4. DOI: 10.3389/frsus.2023.1093911.

ChemicalBook. *1,5-Pentanediol(111-29-5)* ^{1}*H NMR*. Available at: https://www.chemicalbook.com/SpectrumEN_111-29-5_1HNMR.htm.

Di Lorenzo M.L., 2024. Crystallization of poly(ethylene terephthalate): a review. *Polymers*, 16, 1975. DOI: 10.3390/polym16141975.

Foorginezhad S., Zerafat M.M., Ismail A.F., Goh P.S., 2025. Emerging membrane technologies for sustainable water treatment: a review on recent advances. *Environ. Sci.: Adv.*, 4, 530–570. DOI: 10.1039/d4va00378k.

Francis L., Ahmed F.E., Hilal N., 2022. Advances in membrane distillation module configurations. *Membranes*, 12, 81. DOI: 10.3390/membranes12010081.

García-Ávila F., Zambrano-Jaramillo A., Velecela-Garay C., Coronel-Sánchez K., Valdiviezo-Gonzales L., 2025. Effectiveness of membrane technologies in removing emerging contaminants from wastewater: reverse osmosis and nanofiltration. *Water Cycle*, 6, 357–373. DOI: 10.1016/j.watcyc.2024.12.004.

Geens J., Van der Bruggen B., Vandecasteele C., 2004. Characterisation of the solvent stability of polymeric nanofiltration membranes by measurement of contact angles and swelling. *Chem. Eng. Sci.*, 59, 1161–1164. DOI: 10.1016/j.ces.2004.01.003.

Goh P.S., Ismail A.F., 2018. A review on inorganic membranes for desalination and wastewater treatment. *Desalination*, 434, 60–80. DOI: 10.1016/j.desal.2017.07.023.

Grylewicz A., Szymański K., Darowna D., Mozia S., 2021. Influence of polymer solvents on the properties of halloysite-modified polyethersulfone membranes prepared by wet phase inversion. *Molecules*, 26, 2768. DOI: 10.3390/molecules26092768.

Guidotti G., Palumbo A., Soccio M., Gazzano M., Salatelli E., Siracusa V.M., Lotti N., 2024. Fully bio-based blends of poly (pentamethylene furanoate) and poly (hexamethylene furanoate) for sustainable and flexible packaging. *Polymers*, 16, 2342. DOI: 10.3390/polym16162342.

Hassan A., El-Aziz A.A., Elwi M., Klingner A., 2025. Fabrication of Iron oxide nanoparticle loaded recycled PET nanofibers for water purification applications. *Discover Mater.*, 5, 153. DOI: 10.1007/s43939-025-00343-2.

Hu H.-W., Tsao H.-K., Sheng Y.-J., 2024. Impact of nonsolvent–solvent affinity on membrane morphology and microstructure: unraveling the transition from traversing pore to closed void structures. *Macromolecules*, 57, 7640–7653. DOI: 10.1021/acs.macromol.4c01083.

Karayannidis G.P., Nikolaidis A.K., Sideridou I.D., Bikiaris D.N., Achilias D.S., 2006. Chemical recycling of PET by glycolysis: polymerization and characterization of the dimethacrylated glycolysate. *Macromol. Mater. Eng.*, 291, 1338–1347. DOI: 10.1002/mame.200600243.

Karim S.S., Farrukh S., Matsuura T., Ahsan M., Hussain A., Shakir S., Chuah L.F., Hasan M., Bokhari A., 2022. Model analysis on effect of temperature on the solubility of recycling of polyethylene terephthalate (PET) plastic. *Chemosphere*, 307, 136050. DOI: 10.1016/j.chemosphere.2022.136050.

Keirouz A., Galiano F., Russo F., Fontananova E., Castro-Dominguez B., Figoli A., Mattia D., Leese H.S., 2024. Cyrene-enabled green electrospinning of nanofibrous graphene-based membranes for water desalination via membrane distillation. *ACS Sustainable Chem. Eng.*, 12, 17713–17725. DOI: 10.1021/acssuschemeng.4c06363.

Kirshanov K., Toms R., Aliev G., Naumova A., Melnikov P., Gervald A., 2022. Recent developments and perspectives of recycled poly(ethylene terephthalate)-based membranes: a review. *Membranes*, 12, 1105. DOI: 10.3390/membranes12111105.

Lu J., Wu L., Li B.-G., 2017. High molecular weight polyesters derived from biobased 1,5–pentanediol and a variety of aliphatic diacids: synthesis, characterization, and thermo-mechanical properties. *ACS Sustainable Chem. Eng.*, 5, 6159–6166. DOI: 10.1021/acssuschemeng.7b01050.

Ma Y., Zhao X., He B., 2024. Fabrication of nanoparticle array membranes by integrating semi-crystalline polymer self-assembly with NIPS for water treatment. *Nanoscale Adv.*, 6, 3543–3552. DOI: 10.1039/D3NA01157G.

Meticulous Research, 2023. *Membrane Filtration Technologies Market by Type (Reverse Osmosis, Ultrafiltration, Microfiltration, Nanofiltration), Construction, Membrane Material (Polymeric, Ceramic), Sector (Municipal, Residential, Industrial), & Geography – Global Forecast to 2030*. Report ID: MRSE – 104853. Available at: https://www.meticulousresearch.com/product/membrane-filtration-technologies-market-5536.

Milescu R.A., McElroy C.R., Farmer T.J., Williams P.M., Walters M.J., Clark J.H., 2019. Fabrication of PES/PVP water filtration membranes using Cyrene®, a safer bio-based polar aprotic solvent. *Adv. Polym. Technol.*, 2019, 9692859. DOI: 10.1155/2019/9692859.

Moncada J., Dadmun M.D., 2023. The structural evolution of poly(ethylene terephthalate) oligomers produced via glycolysis depolymerization. *J. Mater. Chem. A,* 11, 4679–4690. DOI: 10.1039/D2TA07467B.

Naziri Mehrabani S.A., Vatanpour V., Koyuncu I., 2022. Green solvents in polymeric membrane fabrication: a review. *Sep. Purif. Technol.*, 298, 121691. DOI: 10.1016/j.seppur.2022.121691.

Ndlwana L., Sikhwivhilu K., Moutloali R.M., Ngila J.C., 2020. Heterogeneous functionalization of polyethersulfone: a new approach for pH-responsive microfiltration membranes with enhanced antifouling properties. *J. Membrane Sci. Res.*, 6, 178–187. DOI: 10.22079/jmsr.2019.99706.1238.

Olivares Moreno C.A., Altintas Z., 2022. Bioselective PES membranes based on chitosan functionalization and virus-imprinted nanoMIPs for highly efficient separation of human pathogenic viruses from water. *Membranes*, 12, 1117. DOI: 10.3390/membranes12111117.

Pulido B.A., Habboub O.S., Aristizabal S.L., Szekely G., Nunes S.P., 2019. Recycled poly(ethylene terephthalate) for high temperature solvent resistant membranes. *ACS Appl. Polym. Mater.*, 1, 2379–2387. DOI: 10.1021/acsapm.9b00493.

Ragaert K., Delva L., Van Geem K., 2017. Mechanical and chemical recycling of solid plastic waste. *Waste Manage.*, 69, 24–58. DOI: 10.1016/j.wasman.2017.07.044.

Sahu L.R., Yadav D., Borah D., Gogoi A., Goswami S., Hazarika G., Karki S., Borpatra Gohain M., Sawake S.V., Jadhav S.V., Chatterjee S., Ingole P.G., 2024. Polymeric membranes for liquid separation: innovations in materials, fabrication, and industrial applications. *Polymers*, 16, 3240. DOI: 10.3390/polym16233240.

Schlüter M., Bhutani S., Bahr J., Wohlgemuth K., Held C., 2024. Measurement and PC-SAFT modeling of the solubility of the BHET monomer, the BHET dimer, and PET in single solvents. *J. Chem. Eng. Data*, 69, 1326–1334. DOI: 10.1021/acs.jced.3c00627.

Shakayeva A.K., Yeszhanov A.B., Borissenko A.N., Kassymzhanov M.T., Zhumazhanova A.T., Khlebnikov N.A., Nurkassimov A.K., Zdorovets M.V., Güven O., Korolkov I.V., 2024. Surface modification of polyethylene terephthalate track-etched membranes by 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acrylate for application in water desalination by direct contact membrane distillation. *Membranes*, 14, 145. DOI: 10.3390/membranes14070145.

Sulek M.W., Wasilewski T., 2006. Tribological properties of aqueous solutions of alkyl polyglucosides. *Wear*, 260, 193–204. DOI: 10.1016/j.wear.2005.02.047.

Sun L., Huang L., Wang X., Hu H., Guo J., Zhu R., He S., 2020. Synthesis and structural characterization of sequential structure and crystallization properties for hydrophilic modified polyester. *Polymers*, 12, 1733. DOI: 10.3390/polym12081733.

Tanaka K., Oouchi M., Hayashi F., Maeda H., Waki H., 2016. Structural analysis of the end groups and substructures of commercial poly(ethylene terephthalate) by multiple-WET ^{1}H/^{13}C NMR. *Macromolecules*, 15, 5750–5754. DOI: 10.1021/acs.macromol.6b01105.

Yang G., Xie Z., Cran M., Wu C., Gray S., 2020. Dimensional nanofillers in mixed matrix membranes for pervaporation separations: a review. *Membranes*, 10, 193. DOI: 10.3390/membranes10090193.

Yu S., Li C., Zhao S., Chai M., Hou J., Lin R., 2024. Recent advances in the interfacial engineering of MOF-based mixed matrix membranes for gas separation. *Nanoscale*, 16, 7716–7733. DOI: 10.1039/D4NR00096J.

Zhang M., Ni F., He J., Liu Y., 2021. Evaluation of the formation and antifouling properties of a novel adsorptive homogeneous mixed matrix membrane with in situ generated Zr-based nanoparticles. *RSC Adv.*, 11, 8491–8504. DOI: 10.1039/D0RA10330F.