# Facile Synthesis of Novel Tough and Highly Flexible Biodegradable Membranes for Water Microfiltration

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## Abstract

Microporous polymeric membranes have found great applications in the area of water desalination and wastewater treatment, tissue engineering, drug delivery, and bone regeneration. The ability to create micro-size pores within a polymeric membrane allows for cavity formation that could form channels through which substances may permeate or percolate easily. The majority of these applications though, require micro-size porous membranes with small pore size and narrow pore-size distribution as to allow the control of the permeating substances or tissues. In the current work, an intricate and precise method was developed to generate micro-size porogen salt crystals with controlled micro-size distribution, which is then mixed with a specific biodegradable polymeric blend designed to offer both toughness and high flexibility for the production of microfiltration biodegradable membranes that can withstand the high pressures of large volumes of industrial wastewater undergoing filtration treatment. After casting, the porogen crystals are washed away rendering membranes with well-distributed micro-scale cavities. Using salt porogens offers a great advantage of no contamination to the environment since all salt particles are simply washed away. The ingenuity of this technique is that it allows the filtration of the wastewater at low or no pressures. Copyright © VBRI Press.

Keywords: Microfiltration, biodegradable, polymer blends, porogen microcrystals, wastewater treatment.

### Introduction

Industrial activities in different sectors contribute heavily to squandering precious water resources normally discarded as industrial wastewater [1]. Not only does this process waste important resources for human consumption and agriculture but also it contributes to polluting fresh water resources such as rivers, underground water reserves and fresh water lakes. A massive amount of efforts is currently undergoing to develop advanced technologies for water desalination, purification and treatment. One of these approaches is through the use of biodegradable polymeric membranes for micro- and ultrafiltration [2-4]. Over the past two decades, membrane filtration products (microfiltration or ultrafiltration) have been developed to become the standard for removing suspended solids, colloids and emulsions from every type of water source. Hence, everywhere and anywhere filtration or clarification is required, as membrane microfiltration has the potential to replace conventional flotation, sedimentation, and media filtration processes [5]. Microfiltration (MF) is based on the size exclusion principle with particles in the range of 5  $-10 \mu m$  and

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thus allowing other smaller impurities to pass through as seen in **Table 1** [6].

Table	1.	Various	types	$\mathbf{of}$	pressure	driven	membranes	and	their
general	l ch	aracterist	ics.						

Filtration technique	Pore size (nm)	Common Application	Separating component	Operating pressure (bar)
Reverse osmosis	0.1–1	used in Desalination, and petroleum industries	Metal ions such as (Na <sup>+</sup> , Ca <sup>+2</sup> , Mg <sup>+2</sup> ) and small materials	10–100
Nano- filtration	1–10	Water treatment and softening	Low M.Wt. compounds	10-70
Ultra- filtration	10– 100	Electro- dialysis unit, water purification	Bacteria, proteins, and some viruses	1-10
Micro- filtration	100– 10000	water Treatment, F&B and pharmaceutic industries	Suspended particles, Oil and colloids	0.5-2

Over time, MF has been popular for the removal of other water impurities and has been extensively used for enhancing the removal of natural and synthetic organic matter. MF is also used extensively as a pretreatment to reverse osmosis and nanofiltration. Molecules and particles such as proteins with a molecular weights of 500,000 g/mol and higher, cells, and bacteria can be separated or concentrated with microfiltration. Microfiltration is often used to separate proteins from a pharmaceutical waste. The cells that produced the protein are retained by a microfiltration membrane and the produced protein is allowed to permeate. The ability of MF membranes to efficiently remove bacteria and other microorganisms from a pharmaceutical drug without influencing or damaging the drug itself makes microfiltration membranes the method of choice of sterilization in the biopharmaceutical industry. Comparable to ultrafiltration membranes, fouling or blockage is the most serious problem in microfiltration, limiting the service life of the filter. To optimize the process, prefilters with larger pore sizes (depth filter, etc.) are often used to prevent an early blocking of a final microporous filter. As described before, another essential field of microfiltration membrane have the largest pore sizes (0.1-20 µm) of what are typically called membranes or "guard membrane". These pore sizes overlap with the smaller pores of conventional dead-end filtration techniques [6].

Many techniques are available for the preparation of membranes, including phase inversion, track etching, coating, sintering, and much more [7-11]. Selection of membrane materials is an important criterion when using MF techniques depending on the type of applications it will be used for. For instance, cellulosebased membranes are used for reverse osmosis whereas ether poly(ether ketone). polysulfone and polyvinylidene fluoride-based membranes are for chemical and high-temperature resistant ultrafiltration and microfiltration processes [12-15]. Broad ranges of polymers are utilized for microfiltration membranes such as polysulfone, cellulose acetates, polyamides, PVDF, PTFE, polycarbonates or olefins. Based on the individual characteristics of the polymers, the resulting membranes offer different advantages and disadvantages and have to be selected for the individual application or separation task [16]. Sarah Farrukh and coworkers synthesized polypropylene (PP) blended with thermoplastic polyurethane (TPU) for preparation of microfiltration membranes using thermally induced phase separation (TIPS) technique. The proposed polymers were found compatible with each other and form membranes; properly blended to most importantly, the TPU helped to transform hydrophobic PP membranes into hydrophilic PP-TPU membranes. Water and methanol flux through the fabricated membranes were measured, and it was found that the permeation through the membranes depended upon the type of membrane [17]. For oil and water separation, Jiang et al. used polytetra-fluoroethylene (PTFE) in

combination with an adhesive, dispersant, surfactant and thinner to prepare a superhydrophobic steel membrane [18]. Recently, attention has been paid to biopolymers as film membranes for water treatment due to their biocompatibility and biodegradability answering to a developing environmental concerns and sustainability issues associated with using petroleumbased polymers [4].

One of the most interesting candidates for this type applications is poly(lactic acid) (PLA), a of thermoplastic biodegradable polyester derived from renewable sources [19], and has shown great potential for water treatment applications. PLA is also strong, highly thermally stable with large Young's modulus as compared to other biopolymers. Nevertheless, neat PLA suffers from major drawbacks which limit its use in certain applications. Its stiff nature with less than 10% maximum elongation at break limits its use in applications that need plastic deformation at higher stress levels. Several approaches have been proposed to overcome this limitation. One of these approaches is the incorporation of PLA in polymeric blend with other compatible polymers such as cellulose acetate6 or polyester-based polyurethane (PU).

Polyurethane (PU) is considered a unique polymeric material, as it possesses a wide range of chemical and physical properties. The nature of the dominant soft segments in PU plays a crucial role in its biodegradation [20], Polyether-based polyurethane are usually resistant to biodegradation [21], while polyester-based polyurethane is more likely to be readily biodegradable as almost 75% of the polymer is based on the biodegradable polyester component. The nature of the chain extender and its influence were also studied and it was reported that introducing a chain extender with hydrolysable ester linkage will allow the hard segment comprising the other 25% of the polyurethane to be easily degradable [22-24]. The flexibility of PU could therefore be tailored to produce polymeric samples with controllable hardness and elasticity making it ideal when blended with PLA to produce tough and highly flexible water filtration membranes that can withstand the high pressures of large volumes of wastewater, which is one of the aims of this study.

Regrettably, all the previously mentioned biopolymers form non-porous polymeric membranes, which makes them unfit for wastewater micro- or ultrafiltration. Using porogens to induce porosity in the fabricated membranes may provide an elegant and practical solution for this predicament [25]. A porogen is any mass of a particle of a specific shape and size that can be used to induce pores within a molded structure using the porogen leaching method [26-31]. leaching, also known Porogen as solution casting/particulate leaching is a widely used, facile, convenient, and cost-effective method that can be applied to a wide range of polymers as to induce porosity in the polymer matrix. This method involves the casting of a polymer/porogen solution followed by

solvent evaporation and removal of the incorporated porogen particles by the means of aqueous washing methods. Various porogens, including sodium chloride (NaCl) [26], paraffin spheres [27], sugar crystals [28], gelatin [29], and polymers [30, 31]; have been successfully used to fabricate porous structures. NaCl is perhaps the most widely used porogen. However, the wide variations in its crystal size, lack of interconnectivity, irregular geometry, and its inability to produce submicron and micro-scale pore sizes have limited its use as a porogen in various applications. Therefore, a new type of porogen technology that is more convenient, cost-effective, have a regular geometry and capable of inducing pores with narrow pore size distribution within the polymeric matrix is certainly needed to fabricate membranes with controlled architectures for use in water treatment processes, which is another aim of this study.

In this work, we present a simple, facile and efficient route for the synthesis of porous PLA/PU films using lithium chloride (LiCl) as pore-forming agent (porogen). LiCl is prepared separately using an elaborate preparation method to produce porogen particles with specific uniform micro-size that can be used to afford uniform and precise pores of a particular size. Since the porogen salt particles are highly soluble in water, they are easily removed with simple washing techniques leaving cavities with similar size within the membrane films.

## Experimental

## Materials

Poly(lactic acid) pellets with a commercial name "Ingeo" grade 4043D of density 1.24 g/cc, relative solution viscosity (RV) of 4.0 ( $\pm$  0.10), and D-Isomer level of 4.35% (+/-0.55%) were purchased from Nature Works LLC, Minnetonka, USA and dried under vacuum at 40°C and 600 mbar for 5 hours.

Methylene diisocyantes (MDI), N,N'-Dimethylformamide (DMF) and monoethylene glycol (MEG) were purchased from Aldrich Chemical Co. 2,2'-Oxybis-(N,N-dimethylethylamine) (Niax A99), the blowing catalyst, was supplied from TCL. Triethylene diamine (Dabco EG), the urethane catalyst, and Dabco LK-221, a non-silicon-based surfactant used to improve the emulsification and foam structure stabilization, were supplied from Air Products and Chemicals. Coim G-211 poly(ester)diol, molecular weight 2000 g/mol, was obtained from Coim s.p.u., Italy. Prior to use, MDI was melted at 80°C for 24 h and kept thereafter at 50°C under a nitrogen blanket. The polyol and MEG were heated to 70 °C under vacuum for 18 h to ensure the removal of all air bubbles and water vapor that may otherwise interfere with the isocyanate reactions. The Lithium chloride (LiCl) used as porogen was obtained from fisher chemicals with F.W.42.39 Laboratory grade, USA and the 1, 4- Dioxane (spectrophotometric grade ≥99, Mwt. 88.11) used as solvent in solution preparations was purchased from Tedia, USA. 2-Acetylsalicylic acid (Aspirin) was kindly prepared and supplied by Dr. Nahed Yacob, AUC. All other materials were used as received.

## Material synthesis

## Synthesis of the polymeric and porogenic samples

# Synthesis and spectral analysis of polyester-based polyurethanes

To prepare the PLA/PU base polymeric blends, PLA was purchased as mentioned above whereas the polyester-based PU was prepared as follows. A polyol mixture of the poly(ester)diol, the chain extenders and the various additives was prepared by mixing 57.13 g (0.0285 mol) of Coim G-211 diol, 4.323 g (0.0697 mol) of MEG, 0.3459 g (0.0056 mol) of Dabco EG, 0.1729 g and 0.1729 g of LK-221 surfactant for 20 min using a mechanical stirrer running at a speed of 3000 rpm. The polyurethane polymer was then produced by mixing the polyol blend in a three-necked round-bottom flask fitted with a dry nitrogen inlet and a condenser with a total of 28.3949 g (0.1135mol) MDI at 50°C for few seconds and using a mechanical stirrer running at a speed of 5000 rpm. The weight of MDI was predetermined to ensure the complete conversion of all reactive isocyanate and hydroxyl-functional groups, i.e. index 1. A total of 20 g of the reactive mixture was then quickly poured into a preheated aluminum mold to produce the polymeric sample. Prior to casting, the mold was sprayed with a silicon-based mold release (George Mann Formulated Products). The mold was then placed in an oven heated to 60°C and allowed to stand for 4 h for complete cure. The cured samples were then allowed to stand for 2 days at 25°C prior to evaluating its density determined to be 1.2 g/cm3. FTIR spectra of the prepared PU samples were recorded in room temperature in the transmission mode using a Nicolet FTIR Magna-IR 560 system. PU films for FTIR analysis were prepared by spontaneous evaporation at room temperature of a diluted solution of the polyurethane in DMF placed on a KBr window. The spectra covered the infrared region 4000-400 cm<sup>-1</sup>, the number of scans per experiments was 32 and the resolution was 4 cm<sup>-1</sup>. The IR spectra showed major peaks at 1730 cm<sup>-1</sup> and 1710 cm<sup>-1</sup> corresponding to the free urethane groups and the H-bonded urethane respectively, groups, characteristics of PU microstructure.

### Preparation of the PLA/PU base polymeric blends

Several earlier attempts [6] have been already carried out to test the best PLA/polymer combination for the production of tough and flexible biodegradable membranes. This was done by blending PLA with other biodegradable and/or biocompatible polymers such as CA, PVA, PCL, etc. It was then established that PLA/PU base system provides the best combination. To work out the best composition of a PLA/PU blend that displays the best thermal and mechanical behavior, different polymeric blends with different compositions of PLA and PU, namely, 100/0; 80/20; 60/40; 40/60; 20/80 and 0/100 were prepared using solution casting techniques by dissolving 10g of the total polymer content in 90g 1,4-dioxane using a magnetic stirrer for 24 hours at 60°C to ensure complete and homogeneous mixing. The polymeric solution was then casted on a smooth, free of scratches glass plates using a laboratory-designed applicator. The initial thickness of each film was between 0.8-0.9 mm. The cast films were kept in a closed environment to avoid formation of air bubbles or film deformation. The films were allowed to sit for 24 hours at room temperature and were then subjected to vacuum distillation at 50 °C and 600 mbar for 24 hours to remove any traces of the residual solvent, which otherwise may act as a plasticizer and could eventually distort the film properties.

# Preparation of LiCl porogen crystals of microscale size

Microporous membranes were created in this work using the porogen technique [17]. Due to its high solubility in a variety of polar and non-polar solvents, LiCl microcrystals was chosen as the porogen of choice. Upon washing with water, the microcrystals are easily removed from the polymer matrix leaving behind micro-size cavities in its place of similar sizes without contaminating the polymeric membranes. The main challenge in this technique is the preparation of LiCl NPs and preventing them from any possible coalescence into macroscopic crystals during the preparation. The preparation of stable LiCl NPs was carried out through a recrystallization process of supersaturated aqueous solutions of anhydrous LiCl salt at 35°C. The crystals were formed based on the difference between the solubility and recrystallization. The crystals were collected and dried under vacuum at 80°C to remove all moisture. The collected LiCl NPs crystals were then stored in dry environment to prevent its coalescence into macroscopic ones.

## Preparation of the microporous polymeric membranes

The prepared LiCl NPs were mixed with the PLA/PU 20/80 base system, which exhibited the best mechanical behavior as shown below. The porogen concentrations were 0, 5, 10, 15 and 20% of the total polymer content by mass. Prior to mixing, the porogen NPs were added to 1, 4-dioxane in an Erlenmeyer flask and allowed to sonicate for 10 minutes to ensure homogeneous mixing of the microcrystals within the solvent. During this sonication process, it was observed that the porogen microparticles were easily fractured into smaller microsize crystals as evident by the Malvern Zetasizer method. The microporous membranes were then prepared by casting the solution as described previously. The initial thickness of the cast solution was 1 mm, which was reduced to about 120 µm upon evaporation of the solvent. The glass plates were then immersed in deionized water for 10 to 15 minutes to facilitate peeling off the films and were then washed thoroughly to remove all LiCl NPs to yield the final microporous filtration membranes.

## Characterization methodologies

### Stress-strain measurements

The stress-strain isotherms of the various samples at room temperature were obtained on the dumbbellshaped specimens cut from the cast sheets. Samples free of air bubbles and pinholes that possess specific width, length and thickness of 1.5 cm  $\times$  9 cm  $\times$  0.0085 cm, respectively, were cut from each sample. It was held vertically between two clamps with the lower clamp fixed and the upper clamp suspended from a strain gauge (Statham model G1-16-350). A constant voltage DC power supply (Hewlett Packard 6217) was used to supply approximately 14 volts potential to the transducer and was connected to DS1M12 digital oscilloscope & Waveform generator for output data recording. The transducer was frequently calibrated using a set of standard weights. Its output was found to remain constant over the usual time span of an experiment. Prior to attaching the clamps to a sample, two thin lines were drawn on it. The exact length of the thus-demarcated section of the sample was measured precisely at the desired temperature by means of a cathetometer (Gaertner Scientific Corp., Model M940-303P, precision 1 micron), and the thickness and width were determined with a micrometer. Three measurements each along the thickness and width of the strip were taken, and the average cross-sectional area, A\*, was determined after complete evaporation. The upper clamp was raised to a position giving the desired elongation of the strip in a step-wise fashion.

The distance between the two lines was measured with a cathetometer and recorded as the length L. The ratio of L to  $L_o$  (initial length) presents the elongation (strain),  $\alpha$ . The potential from the stress gauge was calibrated in terms of Newton (N). The stress-strain measurements were made using a sequence of increasing values of the elongation. The equilibrium elastic force, f, was noted after the force reading has become sensibly constant for at least 15 min. The elastic quantity of interest for the stress-strain investigation portion was the nominal stress, f\*, defined by:

$$\mathbf{f}^* = \mathbf{N} / \mathbf{A}^* \tag{1}$$

## Thermogravimetric Analysis (TGA)

TGA experiments were carried out to determine the variation in the thermal degradation temperature of the various films using TGA analyzer (Thermo Scientific - TGA, Q Series). Heating rate of 10oC/min was used to raise the temperature of 10-14 mg samples from room temperature up to 500°C under nitrogen purge flow rate of 50 ml.min<sup>-1</sup>. The precision of the temperature measurement was less than 0.5°C.

#### Scanning Electron Microscopy (SEM)

Scanning electron microscope (Supra 5S LEQ, Zeiss) was employed to study the distribution of the microfiller on the polymer's surface at the Science and Technology Research Center (STRC) at the American University in Cairo. The SEM images were captured by scanning the sample surface with a high energy beam of electrons. The technique of energy dispersive x-ray analysis is used to investigate the elemental composition of the sample which is found commonly on a variety of scanning electron microscopes.

# Microparticle size evaluation using Malvern Zetasizer method

The small size of microparticles is of utmost importance in this work to ensure the creation of microsize cavities within the porous membrane. The Malvern Zetasizer method depends on the use of light scattering, especially dynamic light scattering, and electrophoretic light scattering for measuring the size and zeta potential of dispersed microparticles.

# Porosity and surface area evaluation using BET method

The porosity and surface area of the produced porous membranes were determined by nitrogen gas sorption analysis using an ASAP 2020 analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA). The microporous samples were pretreated by applying vacuum at 40°C for 4 hours. The adsorption and desorption isotherms were recorded using 53-point pressure tables with 20s equilibration intervals. The methods of Brunauer, Emmett, and Teller (BET) and Barrett, Joyner, and Halenda (BJH) were used to calculate the surface area and the micropores size distributions, respectively.

### **Results and discussion**

# Stress-strain measurements of pla/pu blends as the base system

Stress-strain isotherms for neat PLA and PU polymers and the PLA/PU 20/80 blend, chosen as a representative of all the PLA/PU blends, are shown in Fig. 1 by plotting the stress (f\*) against the elongation  $(\alpha)$  for the various samples. It is obvious from the figure that the addition of a large amount (80%) of PU to PLA has improved the mechanical response of the materials tremendously. To further elaborate on these findings, the ultimate properties calculated from the stress-strain results, namely the maximum elongation  $(\alpha_m)$ , maximum nominal force  $(f^*_m)$ , and the maximum energy required to reach maximum nominal stress at maximum elongation (E<sub>m</sub>) for all the investigated samples were calculated and reported as a function of PLA concentration ( $\phi$ PLA) as shown in Figs. 2-4 and listed in Table 2. The energy required to break the samples was calculated by considering the area under

the nominal stress-strain isotherms for the respective samples. The majority rise in the amount of energy required to break the samples is due to the improved flexibility of PLA with the addition of more PU to the blend with a slight decline in the ultimate stress.



Fig. 1. Stress-strain isotherms of various PLA/PU blends.



Fig. 2. The influence of PLA/PU blend composition on the elongation factor  $\alpha$  at maximum.



Fig. 3. The influence of PLA/PU blend composition on the nominal force  $f^*at$  maximum.



**Fig. 4**. The influence of PLA/PU blend composition on the energy required to reach the maximum.

This has probably resulted from the diffusion of the PU chains within PLA chains and thus breaking its coagulation and thus resulting in its marked extensibilities.

 $\label{eq:Table 2. Ultimate mechanical properties of PLA/PU blends with various compositions.$ 

PLA/PU	α <sub>m</sub>	$f_{m}^{*}(N.mm^{-2})$	$E_m$ (J.mm <sup>-3</sup> )
100/0	1.13	36.84	2.50
80/20	1.17	5.28	0.80
70/30	1.19	5.25	0.84
60/40	1.20	3.65	0.50
50/50	1.66	5.19	2.91
40/60	2.34	7.28	7.90
30/70	2.37	8.46	4.98
20/80	2.82	9.80	13.40
0/100	3.85	5.34	9.05

It is obvious from the figures that the PLA/PU 20/80 blend has shown the best mechanical response to increase stress both in terms of toughness and flexibility and therefore it was chosen as the base polymeric system for the development of the microporous membranes.

#### Thermogravimetric Analysis (TGA)

To test and ensure the thermal stability of the polymeric blends, TGA thermograms of the various PLA/PU blend films were generated. The figure clearly shows that the degradation took place between 315°C and 390°C for all samples, which exhibited steady degradation behavior as a common feature. The process of degradation is qualitatively characterized by a set of temperature points on the TGA curve, shown in **Table 3**.

 $\label{eq:Table 3. TGA data of various PLA/PU blends with various compositions.$ 

PLA/PU	T <sub>1</sub> min (°C)	$T_2 \max (^{\circ}C)$
100/0*	315	365
80/20	297	394
60/40	300	394
40/60	301	394
20/80	301	394
0/100**	290	394
*Neat PLA	**Neat PU	•

Upon heating, the sample commences the degradation stage at temperature  $T_1$  and reaches its maximum value at temperature  $T_2$  with weight loss percentage (wt. loss %) at the end of that stage. It is quite interesting to observe the complete conversion of pure PLA sample into all volatile compounds with 0% residue remaining at the end of the thermal degradation process in contrast to other polymeric blends, which left small amounts of residues in a form of incomplete burning of carbon ashes. Among all thermograms, neat

PU showed the highest thermal stability whereas PLA showed the lowest stability and as expected adding PU to PLA improved the thermal stability of the blend. Increasing the ratio of the PU didn't affect the maximum degradation temperature.

### Characterization of microporous membranes

As was mentioned earlier, PLA/PU 20/80 was used as the polymeric base system for the preparation of the microporous membranes. To induce micropores within these films, microsize porogen crystals were used and were then washed away as to create micropores in their place.

### Scanning Electron Microscopy (SEM)

SEM micrograph of the microporous polymeric membrane loaded with 20% porogen microcrystal is shown in **Fig. 5** after complete washing and drying. It was observed from the figures that the pores were evenly distributed in the different matrices, which indicates the complete blending of the porogen crystals with the polymeric chains without creating any agglomerations. This uniform dispersion of the microcrystals has resulted from the apparent use of ultra-sonication during the preparation process.

### Stress-strain measurements

Stress-strain measurements of the developed microporous membranes have been performed in order to evaluate the toughness and flexibility of the membranes as a result of the incorporation and subsequent removal of the porogen microparticles.



Fig. 5. SEM micrographs of PLA/PU 20/80 with 20% porogen concentrations by mass.

To thoroughly examine these aspects of the developed membranes, the ultimate mechanical properties,  $\alpha_m$ ,  $f^*_m$  and  $E_m$  were also evaluated both before washing the porogen particles, i.e. while the membranes still incorporating the porogen microcrystals and after washing them away as shown in

**Table 4.** The table clearly shows that the flexibility of the membranes was not influenced greatly upon the incorporation of the porogen microcrystals while improved upon the incorporation of the micropores following the microcrystals removal.

**Table 4.** Ultimate mechanical properties of microporous membranes having different porogen quantities.

Porogen Content	α <sub>m</sub>	$f_{\mathrm{m}}^{*}(\mathrm{N.mm}^{-2})$	E <sub>m</sub> ( <b>J.mm</b> <sup>-3</sup> )
0	2.82	9.80	13.40
5	2.72	9.44	11.30
10	2.86	11.23	14.60
15	2.93	17.14	22.60
20	2.95	16.75	23.40

The generated micropores has obviously contributed to the ability of the polymeric chains to stretch even further, which increased its extensibilities and improved its flexibility. Quite interestingly, increasing the amount of the porogen microcrystals has also increased the nominal stress possibly due to the filler effect [32-33] of the microparticles which allowed the polymeric chain to be adsorbed on the surface of these micro-filler particles. An interesting observation here is that the nominal stress of the microporous membranes (after washing) also showed an increase in the nominal stress indicating that while the washing process may have removed a large amount of the porogen particles as evident by the SEM, BET and microfiltration experimentations [34], a considerable amount of the microparticles may have still embedded within the polymeric matrix providing added strength to the membrane. This observation continue to hold when considering the influence of the porogen content on the energy required to break the samples as shown in the last two column of the table.

# BET (Brauner, Emett and Teller) porosity measuremen

BET measurements of the synthesized microporous membranes created with different porogen content (after washing) were conducted and used to evaluate.

The BET surface area, pore size and pore volume are shown in **Table 5** and **Figs. 6-8**. The membrane surface area values increased with the increase in the porogen content that created the pores as presented in the second column of **Table 5**. Generally, the addition of the porogen led to an increase in the membrane surface area. This corroborates the porosity results shown in the third and fourth column [**35**]. Interestingly, all the BET parameters have increased with the increase in the porogen content as expected since after washing, a considerable amount of the micro-filler was removed leaving micropores behind. However, further increase in the porogen content has



resulted in a decrease in the porosity parameters with a

maximum at 15% corresponding to the maximum

surface area, pore size and pore volume. This was also

evident with the low amount of hysteresis observed for

these samples during the  $N_2$  isotherm experiment,

**Fig. 6.** BET isotherms for microporous membrane samples containing created using porogen concentrations of 5, 10, 15 and 20%.



Fig. 7. Incremental pore area as a function of the pore diameter for various microporous membranes created using different porogen content.



Fig. 8. Incremental pore volume as a function of the pore diameter for various microporous membranes created using different porogen content.

 Table 5. BET surface area, pore size and pore volume for microporous membranes created with various concentrations of the porogen microcrystals

Porogen (%)	BET surface area (m²/g)	BET Pore Size (nm)	BET Pore Volume 10 <sup>-3</sup> (cm <sup>3</sup> /g)
10	0.187	6.93	1.60
15	0.499	15.9	4.00
20	2.400	3.03	2.00

## Application of the developed microporous biodegradable membranes

To evaluate the microfiltration applicability of the developed microporous biodegradable membranes, a solution of suspended micro-, micro- and macroparticles of Aspirin was filtered out at the low pressure of less than 0.5 bar. While the suspension solution showed great turbidity, the filtrate appeared to be a quite clear solution. Furthermore, to quantify the ability of these microporous membranes to filter micro- and micro suspended particles, zeta-seizer measurements were done to quantity the amount and size of the particles suspended in both solutions. Fig. 9 shows the size distribution by intensity of the Aspirin particles both before and after the microfiltration. It is observed from the figure that the microporous membranes were indeed able to filter out the almost all the suspended Aspirin particles, which confirms the ability of this porous membranes to be used as guard membranes during industrial wastewater treatment.



**Fig. 9.** Size distribution by intensity of suspended Aspirin particles (a) before microfiltration and (b) after microfiltration using the microporous membranes.

#### Conclusion

Industrial activities contribute to the loss of precious water supplies and to the polluting of fresh water resources. In this work, the use of biodegradable polymeric micro-composite membranes in wastewater purification was investigated. The biodegradability of these membranes will ensure the complete dissipation of these materials in a safe and environmentally friendly manner. The utilization of the microfiltration processes will contribute to the removal of all suspended micro- and microparticles from wastewater at low or no pressures. To develop these biodegradable membranes, poly(lactic acid) (PLA) was blended with polyester-based polyurethane (PU) to manufacture the polymeric matrix that combine both high resistance to stress as well as greater range of elasticity. The effect of blending on the thermal behavior of the polymeric matrices was investigated using TGA and showed that blending PU with PLA ensured its thermal stability. Stress-strain isotherms for the various blends showed that PLA/PU 20/80 blend had the most improved mechanical response of the materials. The major rise in the amount of energy required to break the samples was due to the improved flexibility of PLA with the addition of more PU. To induce micropores within these films as to assist in the filtration of industrial wastewater at low or no pressures, porogen microcrystals were used. SEM of all developed membranes of varying porogen content showed even distribution of the pore size within the polymeric matrix. It was interesting to observe that the flexibility of the membranes has increased with the increase in the amount of the pores. Interestingly, all the BET parameters have increased with the addition of more porogen. However, further increase in the porogen content has resulted in a decrease in the porosity parameters with a maximum at 15% porogen content. The N<sub>2</sub> isotherms indicated that the large pore surface area and volume are associated with the smaller pores and thus allowing these membranes to filter out the suspended contaminants. The results conclude that microporous membranes based on PLA/PU 20/80 blend and incorporating 15% porogen microcrystals, after washing and removing the porogen, are suitable for use as guard membranes for the removal of micro-, microand macroparticles from industrial wastewater.

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#### Author's contributions

All authors have contributed to the work plan. RA has synthesised the polyurthenae materials, performed all spectral analyses and structural illucidation. AH has ran all membrane preparation and characterization. AZ and TM have performed the results interpretation. All authors contributed to writing the manuscript in its current form. Authors have no competing financial interests.

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