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Abstract

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Superomniphilic Poly(glycerol sebacate)- poly(L-lactic acid) Electrospun Membranes for Oil Spill Remediation

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Abstract: Superomniphilic materials are defined as materials that can uptake both water and oil-like liquids. In this study, a facile method to prepare a superomniphilic and biodegradable core-shell structure of poly(glycerol sebacate) (PGS) and poly(L-lactic acid) (PLLA) is reported. The developed method immobilizes the PGS polymer onto the surface of the PLLA electrospun fibers, increasing the presence of hydroxyl groups on the surface of the membranes. The sample with 25 wt% PGS can uptake polar and apolar solvents, and presents a superhydrophilic behavior. The PGS:PLLA composite is reusable up to 10 cycles of solvent (water or organic solvents) absorption with a separation efficiency of 99.5%, and its general appearance resembles the first absorption/compression cycle. Finally, this work presents a novel biodegradable polymeric blend membrane with superomniphilic properties, produced

by a scalable process, which could be easily implemented to fight against environmental disasters such as large area oil spills.

Keywords: poly(L-lactic acid), poly(glycerol sebacate), superomniphilic, electrospinning, chemicals spill cleaning

1. Introduction

Intensive research in designing novel universal absorbent materials and processes for containment of oil spills, and for an efficient oil and water separation, is currently being performed ^[1]. The materials available to remediate oil spills, are either superhydrophilic or superoleophilic that enable complete separation of apolar fluids from water.

Superomniphilic materials are materials that have superhydrophilic and superoleophilic properties, i.e., an apparent contact angle of 0° when placed in contact with water or any other solvent ^[2]. “Universal” sponges and pads, based on cellulose, polypropylene and polyesters, are sold as products capable to absorb solvents with different polarities, ranging from water to apolar oils. Nevertheless, the amount of solvent that these solutions can uptake is usually limited to 1:1 (solvent : polymer mass) ^[1]. In that sense, the development of materials capable to quickly absorb higher amounts of any solvent spill, independent of their viscosity or polarity is a challenging demand.

Usually, the processing techniques used to obtain highly porous polymeric membranes and sponges are extremely complex and involve the use of polymeric synthesis, and curing procedures. Chatterjee et al. ^[1] prepared microporous polymer sponges by ice templating of polyethylenimine in aqueous solutions, followed by cross-linking. In their work, they showed that the omniphilic behavior of the developed sorbents depends on the chemical modification during polymer synthesis. Bong et al. ^[3] developed a selective gas-water-oil porous filter

using three-dimensional graphene structures, using oxygen plasma treatment, with self-assembled (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane to tune the wetting properties of the developed sponges. Plasma treatment is one of the most conventional methods to modify the surface properties and enhance hydrophilicity of polymeric membrane surface, however its application hinders the size of sponges to the laboratorial scale ^[4].

Recently, natural and synthetic polymeric electrospun fibrous membranes are emerging as the new generation of superhydrophobic and oleophilic materials for oil spills remediation. Patowary et al. ^[5] reported that electrospun silk fibres modified with octadecylamine presented superhydrophobic features (WCA of 150°), and good engine and crude oil absorption ability. Polyurethane (TPU) electrospun membranes functionalized with poly(N-isopropylacrylamide) (PNIPAM) was prepared by Ou et al. ^[6]. PNIPAM is a thermoresponsive polymer that changes its wetting behavior when the temperature increases above 40 °C. Another alternative to tune the wettability of such membranes is blending polyhedral oligomeric silsesquioxane (POSS) with hydrophobic and oleophilic polymers. The presence of POSS on the surface of the polymer fibres enhances the hydrophobic behavior of the polymeric substrate, without compromising its oleophilic behavior ^[4, 7].

Recent studies have shown the potential of hydrophobic and oleophilic electrospun membranes for the oil/water separation ^[8]. Nevertheless, the use of superhydrophilic and selective membranes for oil spills remediation, especially in large areas, remains a scientific challenge. In the present work, a superomniphilic membrane was developed by mixing two biodegradable polyesters, poly(L-lactic acid) (PLLA) and poly(glycerol sebacate) (PGS) in a compatible solvent. The solution was electrospun into a grounded collector and random oriented fibre mats were obtained. The influence of the PGS ratio on the wettability properties of the blend in the presence of different, polar and apolar solvents was

systematically addressed. The materials developed showed a remarkable superomniphilic behavior, with great potential to be used for large area oil spills remediation.

2. Results and Discussion

2.1. Morphology of the PLLA-PGS Membranes

Polymeric PLLA-PGS fibres were prepared by blending the polymers in the same solvent solution, followed by processing via electrospinning. Pristine PLLA membranes present a smooth cylindrical shape, without the presence of beads (**Figure 1a**). When the PGS prepolymer is added to the electrospinning solution, it was observed the presence of small beads around the PLLA fibres for the sample with 25 wt% of PGS prepolymer (Figure 1b). Furthermore, when the amount of prepolymer was increased to 40 wt%, the membrane presented cylindrical fibres identical to the ones observed for the pristine PLLA (Figure 1c). Further, increasing the amount of PGS prepolymer in the electrospun solution led to the presence of fibres mixed with some regions where the PGS prepolymer formed a thin film layer on the surface of the membrane (Figure 1d).

Figure 1: PLLA-PGS prepolymer electrospun samples morphology: a) C0 (PLLA), b) C25 (25 wt% PGS), c) C40 (40 wt% PGS) and d) C50 (50 wt% PGS).

In this work, the PLLA was used as a template to drag and mechanically support the PGS prepolymer during the electrospinning process. After processing, the PGS prepolymer needs to be cured at high temperatures and low pressure, to form a stable three-dimensional cross-linked network^[9]. In that sense, the curing procedure was applied not only to the PGS:PLLA fibres, but also to the PLLA pristine membranes (**Figure 2a**). After annealing at 120 °C under low pressure for 48 h, the fibres presented sections with different diameters, due to the recrystallization of the polymer resulting in macroscopic shrinkage of the sample. PLLA is a slow crystallizing polymer, with a glass transition above the room temperature, and samples electrospun at room temperature often reorganize in the amorphous state^[10]. The annealing process supplies enough thermal energy to promote segmental diffusion and reorganization of the polymer chains, increasing sample crystallinity, and releasing internal stresses generated during the processing^[10b, 11]. Furthermore, the samples with 25 wt% of PGS presented an

interconnected porosity with smoother surface fibres, compared to the uncross-linked sample. Moreover, it was observed that when the amount of PGS increases (C40 and C50), the PGS starts to form a continuous film in some regions of the sample, increasing in area with the amount of PGS polymer present in the final sample composition (Figure 2c and d). Following the curing process, it was also observed that the elastomeric polymer wraps around and completely covers all the surface area of the PLLA fibre (Figure 2e and f) in the 25 wt% PGS sample. Also, present hollow fibres around the edges of the fibre mats, a clear indication that the PLLA forms a fibre template which drags and supports the PGS prepolymer in a core-shell structure, with the PLLA fibres making up the core, and shell comprised of the PGS elastomer.

As-spun PLLA fibres presented an average diameter of 616 ± 161 nm, and after annealing at 120°C , an increase in the average fibre diameter up to 688 ± 197 nm was observed, probably due to the chain reorganization that occurs during the annealing process ^[10a]. Further, when the PGS prepolymer is added to the electrospun solution a dual behavior was observed. For lower concentrations of PGS pre-polymer (≤ 25 wt%), the fibre average of the core-shell fibre membrane increased up to 750 ± 184 nm, but for higher concentrations of prepolymer (40 wt% PGS), the fibre average decreased to 455 ± 134 nm. This is likely due to changes in the solution charge density induced by PGS prepolymer, that is able to ionize and carry more electrical charges, and consequently stretch the droplet even further, leading to a decrease of the polymer average fibre diameter ^[12]. After cross-linking, the sample with 25 wt% PGS suffers a reduction of the average fibre diameter down to 627 ± 190 nm, which could be assigned to the evaporation of water contained inside the prepolymer, and the network, resulting from the cross-linking procedure.

Usually, core-shell electrospun polymer fibres are obtained using a two-fluid coaxial spinneret, where one polymer fluid is fed in the core of the needle and the other polymer

flows on the outer layer of the coaxial needle, or spinning from emulsions, where the surface energies of the two different polymeric solutions are the driving force for the spontaneous organization into a core-sheath fibre structure ^[13].

Xu et al. ^[14] prepared PGS:PLLA core-shell fibres through the use a coaxial spinneret, where the outer layer was the PLLA and the core was made of PGS prepolymer. In their work, the core fibres produced had an average fibre diameter in the range 2 - 5 μm , and presented bonded fibres due to the cross-linking of the PGS sheath. In our work, by blending the PGS prepolymer and the PLLA in the same solvent solution, bicomponent fibres were obtained, where the core was PLLA and the sheath was made of PGS, in opposition of the work reported by Xu et al. ^[14]. By basing our preparation on a single needle the method is versatile, reproducible and can be readily upscaled without losing its features.

Figure 2: PLLA-PGS polymer fibre morphology after curing at 120 °C during 48 h SEM images: a) C0 (PLLA), b) C25 (25 wt% PGS), c) C40 (40 wt% PGS), d) C50 (50 wt% PGS), e) detail of PLLA fibre surface and f) the cross section of the PLLA-PGS (C25).

2.2. Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy in Attenuated Total Reflectance (ATR) mode was performed to the cured PGS:PLLA samples, and pristine materials. PLLA presented an absorption band at 1757 cm^{-1} ($\text{C}=\text{O}$) attributed to the amorphous regions of the polymer

chains, and the characteristic absorptions band of the α and α' can be observed at 1183 cm^{-1} ($\nu_{as}(C-O-C) + r_s(CH_3)$) and 1092 cm^{-1} ($\nu_s(C-O-C)$)^[10]. The FTIR spectra of the PGS cross-linked film present an absorption band at 1736 cm^{-1} , corresponding to the stretching of the carbonyl ester^[15], the absorption band at 1185 cm^{-1} was attributed to the in-plane bending vibration of C – O bonds^[16]. The characteristic absorption bands of the pristine polymers were observed in the PGS:PLLA blended fibres, and no new absorption mode appeared or was totally suppressed, which suggests that the polymers are immiscible (**Figure 3**). It was observed that the absorption band at 1757 cm^{-1} (PLLA) broadens with the incorporation of the PGS polymer due to the overlap of the carbonyl absorption band of PLLA (1757 cm^{-1}) and the carbonyl ester from the PGS polymer (1736 cm^{-1} , Figure 3).

Figure 3: Infrared spectroscopy of for the PLLA-PGS membranes.

To further corroborate that the shell layer is made mainly from the PGS cross-linked polymer, XPS analysis was performed. **Figure 4a** shows the XPS full spectra for the PLLA, PGS:PLLA (C25) electrospun membranes and PGS elastomeric film, and exhibits two main peaks located at binding energies of 285 eV and 531 eV, corresponding to C1s and O1s,

respectively. Figure 4b shows the C1s spectra for the PLLA electrospun fibres annealed at 120 °C during 48 h, that simulates the curing procedure of the PGS polymer. The C1s peak was separated in three components of approximately the same composition, corresponding to the three steps of the carbon atoms present in PLLA. The C1 signals were attributed to the C – C, C – O and O – C = O bonds, located at 284.5 eV, 286.5 eV and 289.2 eV, respectively. Almost same C1s profile can be observed for the PGS film, however, the ether (C – O) and ester (O – C = O) have different intensities (Figure 4c), when compared to the PLLA sample. The sample with the shell structure made of PGS (C25) presented a C1s spectra like the pristine PGS material (Figure 4d). **Table 1** summarizes the XPS analysis for the atomic composition and C/O atom ratios for the PLLA, PGS and core-shell fibres of PGS:PLLA. The XPS suggests that the PGS shell has an heterogenous thickness distribution, probably due to the high surface roughness of the PGS polymer, as observed in Figure 2f.

Figure 4: XPS spectra of the electrospun PGS-PL membranes: a) Full spectra for the C25 sample, b) C1s spectra for C0 (PLLA), c) C1s spectra for C100 (PGS film) and d) C1s spectra for C25 (25 wt% PGS electrospun membrane).

Table 1: X-ray photoelectron spectroscopy (XPS) analysis of PGS:PLLA blends.

Sample	XPS C1s envelope ratios			C/O ratio (%)
	(%)			
	C - C	C – O - C	O – C=O	
C0	42.55	26.97	30.48	2.04
C25	48.29	32.57	19.14	2.43
C100	53.04	35.55	11.42	3.31

2.3. Solvent Absorption by the Membranes

2.3.1. Water and Oil Wettability

The surface wettability of the PLLA membrane was assessed by placing a drop of water (with blue dye) and engine oil (red coloured) on the surface of the samples (**Figure 5**). PLLA presented a strong hydrophobic behavior in the presence of water, with a water contact angle (WCA) of $126 \pm 2^\circ$ (**Table 2**). The value measured was in accordance to the ones reported previously, and this behavior was attributed to the large sub-micron range roughness produced by the electrospinning process, and due to the fibrillar structure of the membranes [17]. On the other hand, when a drop of engine oil is placed onto the surface of the PLLA membrane, the droplet is immediately uptaken by the sample, indicating the oleophilic character of the fibre membrane (Figure 5). Furthermore, pure PGS films were prepared and their wettability behavior against water and oil was performed. It was observed that PGS films show a hydrophilic behavior, with a WCA of $42 \pm 2^\circ$. When the drop of oil is placed

onto its surface, the contact angle decreases to $7 \pm 1^\circ$ (Table 2), revealing a strong oleophilic behavior.

When the PLLA and PGS are blended in the solvent solution and electrospun together, followed by the PGS curing procedure, it was observed that the materials could immediately absorb the water drop, as well as the engine oil, conferring to the PGS:PLLA blends a superomniphilic behavior, that is, $\theta_{adv}^* = \theta_{rec}^* \cong 0^\circ$, for both, water and engine oil (Table 2).

Figure 5: Images of the water (blue droplet) and engine oil (red droplet) on the surface of: a) PLLA, b) C25, c) C40 and d) C50 membranes.

Table 2: Water contact angle (WCA) and oil contact angle (OCA) of all the prepared samples.

Samples	WCA (°)	OCA (°)	Porosity (%)	Specific
				surface Area (m ² .g ⁻¹)
C0	126 ± 2	N/A	87 ± 4	1683
C25	N/A	N/A	93 ± 4	2009
C40	N/A	N/A	86 ± 6	471
C50	N/A	N/A	76 ± 4	779
C100	42 ± 2	7 ± 1	0	*

This remarkable superomniphilic behavior of the electrospun PGS:PLLA blended samples is probably due to the presence of the PGS on the surface of the fibres (Figure 2), increasing the amount of hydrophilic hydroxyl groups on the membrane surfaces ^[18] (Table 1). These regions of PGS can uptake the solvent molecules (water or engine oil) on the surface of the fibres, after which the liquid sinks by capillary effect, being stored in the porous bulk structure of the electrospun membrane.

The specific surface area was measured for the developed pristine (PLLA) and blends of PGS:PLLA electrospun fibres. It was observed that the electrospun PLLA template presents a specific surface area of 1683 m².g⁻¹, and when the PGS was added to the electrospun solution, an increase of the specific surface area up to 2009 m².g⁻¹ was observed for the sample with 25 wt% PGS. When the amount of PGS presented in the blend increases to concentrations higher than 25 wt%, the specific surface area decreases (Table 2), probably due to the presence of small PGS agglomerates (Figure 2), reducing sample overall porosity (Table 2). For lower PGS concentrations (≤ 25 wt%), it was observed a reduction in fibre average diameter (627 ±

190 nm) of the blended electrospun samples (Figure 2), when compared to the PLLA template (688 ± 197 nm), and consequently an increase of the specific surface area available in the blended samples was detected (Table 2).

The overall porosity of the prepared samples was measured by the pycnometer method. It was observed that the porosity of the samples increased for PGS contents up to 25 wt%, which is probably due to the decrease of the average fibre diameter, observed for the blended samples. For higher amounts of PGS, the overall sample porosity decreases, which could be due to the increasing presence of small elastomeric agglomerates across the sample (Figure 2).

2.3.2. Solvent Absorption Stability

The ability of the developed membranes to absorb different solvents was then evaluated (**Figure 6**). Polar solvents (water and formamide) and apolar hexane, as well as commercial vegetable and engine oil, were chosen to study the uptake capability of the PGS:PLLA membranes. Clean, vacuum dried samples were immersed in the liquid and the amount of solvent that the sample could absorb was calculated as the ratio of absorbed solvent to the dry weight of the membrane. It was observed that PLLA had a strong hydrophobic behavior and no water could enter in the porous spaces of the membrane. Furthermore, PLLA membranes revealed a remarkable capability to uptake hexane, formamide, engine and vegetable oil (Figure 6a).

When the PGS is blended with PLLA, it wraps the PLLA fibre surface (Figure 2), and an interesting uptake behavior was observed for the different solvents. The polymer blended fibres were now able to uptake not only the chemical solvents, but also water, and the amount of liquid that could be entrapped by the membrane depends on the amount of PGS added to the PLLA-PGS solution. For PGS contents up to 25 wt%, all solvent uptake was analogous to previously observed for the PLLA, but a water uptake up to ≈ 7 times its dry weight was

noticed (Figure 6a). With an increase of PGS content, the amount of solvent that the sample can uptake decreases, which is probably due to the PGS agglomerates that appeared on the surface of the membranes (Figure 2), reducing the membrane overall porosity and specific surface area (Table 2), halt the material capability to entrap solvent.

Thoroughly vacuum dried samples were immersed in solvent for 10 min to ensure equilibrium absorption, and the weight of the solvent-swollen sample was measured carefully wiping excess solvent of the membranes with a tissue paper. The absorption capacity was calculated as the ratio of absorbed solvent to the dry weight of the membrane. Before each cycle, the solvent was squeezed to expel the entrapped solvent. Subsequently, the sample was immersed in the solvent and the uptake in the next cycle of absorption was measured. For each pair sample – solvent, it was measured at least ten uptakes – compression cycles. Furthermore, no systematic changes in solvent absorption, over the 10 experimental cycles were detected (Figure 6).

The membranes have discrete pores of 10 – 50 μm in diameter, disorderly distributed in the surface with numerous randomly oriented grooves of about 10 μm in width (Figures 1 and 2). Capillary action draws the wetting fluids into the pores and the polymeric walls can also adsorb solvent. While PLLA membranes have a strong hydrophobic behavior when water is placed onto the surface of the fibres; the PGS polymer added to the surface of the PLLA fibre template can decrease the WCA of the membrane due to the presence of a higher concentration of the hydroxyl groups, and the electrospun sample behaves as omniphilic, with a WCA of $\approx 0^\circ$ (Figure 6). The sample with 25 wt% of PGS in the starting blend solution showed an uptake performance and cyclability analogous to the PLLA membrane for the different organic solvents tested, and modifying the water wetting properties of the blended membrane to uptake water. In that sense, the materials developed in this work, can be denominated superomniphilic materials.

Figure 6: Solvent absorption capacity for the different PGS:PLLA membranes (a), membrane uptake recorded during 10th cycles for (b) water, (c) hexane, (d) engine oil. Morphology of the C25 sample after the 10th cycle of (e) engine oil absorption and (f) vegetable oil absorption. The arrows highlight the evolution of water uptake for the C0 and C25 electrospun samples.

2.3.3. Oleophilicity of the Membranes in Presence of Water

For oil spills remediation, were the oil phase must be removed, and leaving behind clean water, the ability to selectivity absorb oil in the presence of water is an important feature. In this work, as a proof of concept, water and engine oil (transparent and red dyed phase in

Figure 7, respectively) were mixed. The solution was kept under stirring, and a dry piece of membrane was placed inside of the solution for 60 s, removed, compressed to release all the liquid, and immersed again in the solution (see video in supporting information), until complete removal of the engine oil (Figure 7, red phase), to make the process feasible, as simple as possible, and ready to be applied under real oil spill conditions. In the end of the process, no visible oil exists in the water phase (Figure 7), and the separation efficiency was higher than 99.5%.

Figure 7: Oil/water separation by C25. (a) At the start of the absorption, (b) at the 5th absorbing cycle, (c) at the 10th cycle and (d) after complete absorption after 14 cycles.

3. Conclusions

This study demonstrated the facile, cost effective and environmental friendly synthesis superomniphilic core shell PGS:PLLA fibre membranes. The PGS shell layer creates a unique superomniphilic fibrous membrane with a higher concentration of hydrophilic

hydroxyl groups, capable to uptake polar, and non-polar solvents, with different surface tensions, densities, or viscosities, including engine and vegetable oils. The presence of hydroxyl groups on the surface of the membranes provides selectivity for oil absorption, leaving behind clean and clear water. The sample with 25 wt% of PGS presented a solvent uptake capability like the pristine PLLA fibres, with the advantage that they also behave as superhydrophilic membranes. Even after 10th absorption/compression cycles, the membrane presented a separation efficiency of 99.5%, and general appearance was like the first absorption/compression cycle. This work presents a novel biodegradable polymeric blend membrane with superomniphilic properties, produced by a scalable process that could be easily implemented to fight against large area oil spills.

4. Experimental Section

Materials: Poly(L-lactic acid) (PLLA, Purasorb PL18, M_w = 217 – 225 kDa) was acquired from Corbion Netherlands and glycerol, sebacic acid, N,N-dimethylformamide (DMF), dichloromethane (DMC), hexane and formamide, all analytical grade, were purchased from Sigma-Aldrich (Australia). Water-based food dye and vegetable oil were purchased from Woolworths (Australia) and oil-based food dye from Spotlight (Australia).

PGS Synthesis: PGS prepolymer was prepared following the method described elsewhere ^[9]. Briefly, equimolar of glycerol and sebacic acid were mixed in the flask to heat at 120 °C under argon atmosphere for 24 h. After, the prepolymer was poured into a Teflon petri dish and placed inside an oven (Shel Lab 1401D) at 120 °C under vacuum during 48 h, to induce the cross-linking of the sample.

Membrane Processing: Poly(L-lactic acid) and PGS prepolymer in different weight ratios (**Table 3**) were dissolved in a co-solvent system of DMF and DMC (3/7 v/v) to obtain a solution with a final polymer concentration of 10 %wt. The solution was prepared at room

temperature with the help of a magnetic stirrer until complete dissolution of the polymer, and placed in a glass syringe (10 ml) fitted with a steel needle of 500 μm inner diameter. Electrospinning was conducted at 1.0 kV.cm^{-1} with a high voltage power supply from Gamma High Voltage. A syringe pump (from KDSscientific) was used to feed the polymer solutions into the needle tip at 0.5 mL.h^{-1} . The electrospun fibres were collected in a ground collecting plate placed at 15 cm apart from the needle. All experiments were conducted at $21 \pm 2 \text{ }^{\circ}\text{C}$ and a relative humidity of $43 \pm 5\%$. After, the samples were submitted to cross-linking in the same conditions as the pristine PGS film, detailed above. Moreover, the PLLA fibres were submitted to the same annealing process used to cross-link the PGS prepolymer.

Table 3: Sample identification and formulation prepared in this work.

Sample identification	Mass ratio of PGS: PLLA
C0	0 %wt PGS
C25	25 %wt PGS
C40	40 %wt PGS
C50	50 %wt PGS
C100	100 %wt PGS

Sample Characterization: Electrospun samples were coated with a thin layer of platinum by magnetron sputtering (Dynavac sputter coater), and their morphology (surface and cross-section) was analyzed by scanning electron microscopy (JEOL JSM-7500). Fibre average diameter and distribution were calculated over approximately 50 fibres using the SEM images (1000X magnification) and the ImageJ software^[19]. Fourier transform infrared (FTIR) spectroscopy in Attenuated Total Reflectance (ATR) mode was performed at room temperature, between $4,000 - 600 \text{ cm}^{-1}$, collected after 32 scans with a resolution of 2 cm^{-1} .

Sample wettability was determined by measuring the contact angle of ultra-pure water (Millipore) and vegetable oil using an OCA 20 Dataphysics apparatus. At least five measurements were performed in different places, for each of the liquids used and the value is presented as an average $\pm$ standard deviation.

Specific surface area was measured by NOVA 1000 high speed gas sorption analyzer. Each sample of around 4 mg was placed in the tube of the analyzer to degas at 40 °C for 15 h. The tube was then put into argon for the specific surface area determination by NOVA 1000 analyzer.

Membrane overall porosity was determined by the pycnometer method following the procedure described elsewhere^[20]. Briefly, the weight of the pycnometer filled with ethanol was measured and labeled as W_1 ; the sample with weight W_s was immersed in the filled pycnometer. Subsequently, the sample was saturated by ethanol; additional ethanol was added to complete the volume of the pycnometer. Then, the pycnometer was weighted and labelled as W_2 ; the sample filled with ethanol was taken out of the pycnometer and the residual weight of the ethanol and the pycnometer was labelled as W_3 . The porosity of the membrane was calculated according to:

$$\varepsilon = \frac{W_2 - W_3 - W_s}{W_1 - W_3} \quad (1)$$

The mean porosity of each membrane was obtained as the average of the values determined in three samples.

Solvent Absorption and Removal Behavior: Samples with 30 x 30 mm² were immersed in different solvents (water, hexane, formamide, vegetable and engine oil). After 5 min immersion, the samples were removed from the solvent and gently soaked up with filter

paper to remove the excess of solvent. The degree of swelling was assessed by measuring the difference between dry and swollen samples, and calculated according to:

$$\text{Degree of swelling (\%)} = \left[\frac{W_s - W_d}{W_d} \right] * 100 \quad (2)$$

where, W_s is the mass of the swollen sample, and W_d is the initial dry mass.

The uptake stability of the samples was measured by repeating the procedure described previously, but before each measurement, the sample was squeezed to remove the higher amount of solvent possible, and then the weight of the sample was acquired before and after solvent immersion. The oil removal efficiency was determined according to:

$$\text{Oil removal efficiency (\%)} = \left[\frac{W_i - W_f}{W_i} \right] * 100 \quad (3)$$

where, W_i is the initial weight of oil in the oil-water mixture, and W_f is the final weight of the oil in the mixture. Finally, the surface of the samples after immersion in vegetable oil was characterized by SEM (JEOL JSM-6490LV).

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Figure and Table Captions

Figure 1: PLLA-PGS prepolymer electrospun samples morphology: a) C0 (PLLA), b) C25 (25 wt% PGS), c) C40 (40 wt% PGS) and d) C50 (50 wt% PGS).

Figure 2: PLLA-PGS polymer fibre morphology after curing at 120 °C during 48 h SEM images: a) C0 (PLLA), b) C25 (25 wt% PGS), c) C40 (40 wt% PGS), d) C50 (50 wt% PGS), e) detail of PLLA fibre surface and f) the cross section of the PLLA-PGS (C25).

Figure 3: Infrared spectroscopy of for the PLLA-PGS membranes.

Figure 4: XPS spectra of the electrospun PGS-PL membranes: a) Full spectra for the C25 sample, b) C1s spectra for C0 (PLLA), c) C1s spectra for C100 (PGS film) and d) C1s spectra for C25 (25 wt% PGS electrospun membrane).

Figure 5: Images of the water (blue droplet) and engine oil (red droplet) on the surface of: a) PLLA, b) C25, c) C40 and d) C50 membranes.

Figure 6: Solvents absorption capacity for the different PGS:PLLA membranes (a), membrane uptake recorded during 10th cycles for (b) water, (c) hexane, (d) engine. Morphology of the C25 sample after the 10th cycle of (e) engine oil absorption and (f) vegetable oil absorption.

Figure 7: Oil/water separation by C40. (a) At the start of the absorption, (b) at the 5th absorbing cycle, (c) at the 10th cycle and (d) after complete absorption after 14 cycles.

Table 1: X-ray photoelectron spectroscopy (XPS) analysis of PGS:PLLA blends.

Table 2: Water contact angle (WCA) and oil contact angle (OCA) of all the prepared samples.

Table 3: Sample identification and formulation prepared in this work.

Large area oil spill is becoming an increasing threat to environment. Superomniphilic electrospun membranes with core-shell structure have been prepared by a scalable process. Presented with the capability of selectively absorbing oil, the membrane can be reused for at least 10 cycles with a separation efficiency of 99.5% and with consistent absorbing performance.

Chemicals spill cleaning

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Superomniphilic Poly(glycerol sebacate)- poly(L-lactic acid) Electrospun Membranes for Oil Spill Remediation

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Supporting Information

Superomniphilic Poly(glycerol sebacate)- poly(L-lactic acid) Electrospun Membranes for Oil Spill Remediation

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Selective oil absorption.zip

The video shows the selective oil absorption of the superomniphilic polymeric membrane in a real case. The membrane can be used repeatedly to absorb oil from water.