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Surface properties evolution in electrospun polymer blends by segregation of hydrophilic or amphiphilic molecules

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ABSTRACT: Polymer blending can be used as a one-step surface modification technique to alter the wettability of electrospun mats. In this work, blends of hydrophobic thermoplastic elastomer SEBS with hydrophilic PEO or amphiphilic PEO-PPO-PEO were prepared and the resulting surface properties investigated. The low surface energy PPO block drove the segregation of the amphiphilic polymer and hydrophilization was achieved in aqueous medium. Surprisingly, surface segregation continued at room temperature during weeks after processing. The expected equilibrium blend morphology is discussed to explain the ageing results. In addition, the effect of different matrices on the mobility of the amphiphilic molecules was analyzed by comparing the segregation of PEO-PPO-PEO in rubbery SEBS and rigid PS. The low glass transition temperature of SEBS increased the free volume fraction at room temperature and facilitated the segregation.

KEYWORDS: electrospinning; blends; amphiphilic; surface modification; wettability.

INTRODUCTION

Surface modification of polymers is especially interesting for structures with high surface area-to-volume ratio such as electrospun mats, allowing the adjustment of surface properties without compromising the bulk properties. Hydrophilization is one the possible desired outcomes of surface modification, important for applications in which interaction with an aqueous medium is expected. Examples include hydrophilic tissue engineering scaffolds with enhanced cell attachment and proliferation[1], or antifouling hydrophilic surfaces composed of polyethylene oxide (PEO) groups at the surface that can prevent protein adsorption[2].

Many post-electrospinning treatments such as coating or plasma are used for this purpose, not only adding cost and time but sometimes failing to produce a homogeneous treatment on deeper fiber layers[3]. Alternatively, the incorporation of nanoparticles or other polymers (by blending) into the electrospinning solution can alter the surface properties of the fibers before the deposition and therefore result in a more homogeneous surface treatment throughout the nonwoven mat. Blending, in particular, established as a way to change bulk properties, can also be used as a surface modification technique considering that the blend morphology at the surface can be different from the bulk[4].

To achieve hydrophilization by blending two alternatives are possible: mixing the hydrophobic matrix with either a hydrophilic or an amphiphilic polymer[5]. Examples of the former include blends with poly(vinyl alcohol) (PVA)[6-9], poly(vinyl methyl ether) (PVME)[10] or poly(glycolic acid) (PGA)[11], while examples of the latter can be found in recent studies on the hydrophilization of different hydrophobic polymers using the amphiphilic block copolymer

poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-PPO-PEO) with great surface segregation[12-14].

However, it is still unclear how the morphology of these electrospun blends evolves and if the surface modification is achieved only through the segregation of phase-separated structures, like droplets, or also by isolated molecules. Some immiscible blends can present a complete wetting layer as the equilibrium morphology, for example, while the surface of miscible blends can be enriched with the modifying molecules. Energy effects play a major role on surface segregation during blending: the component with low surface energy tends to segregate to the solid/air surface while higher surface energy components tend to be immersed in the matrix [15, 16]. From this perspective, hydrophilic polymers like polyethylene oxide (PEO) are not a good choice due to their high surface energy that can hinder segregation. Annealing in an aqueous environment can help the segregation of hydrophilic polymers[17]. In the case of amphiphilic molecules like PEO-PPO-PEO block copolymers, the idea is that the lower surface energy block (PPO) will segregate to the air surface and drag the hydrophilic blocks (PEO), which will hydrophilize the surface once a contact with an aqueous medium is established [18-20]. Still, some studies revealed that entropic factors related to the molecular weight of the blended polymers may overcome energy factors and favour the segregation of higher energy components to the surface[21, 22].

In electrospinning, the rapid processing can “freeze” the microstructure in a state out of its thermodynamic equilibrium. A thermal treatment like annealing can resume the blend morphology evolution towards the equilibrium and, like mentioned above, a wetting layer or a more enriched surface may be formed after processing. The concept is that treating the matrix above its glass transition temperature increases its free volume fraction and the mobility of the

second phase with lower surface energy, which may continue to segregate to the surface[4, 23]. Another possibility is that the post-processing segregation can occur even at room temperature over longer periods of time. Migration over months of small molecular weight polyethylene glycol (PEG) molecules inside a polyethylene terephthalate (PET) matrix have been recently reported[22]. There are also questions regarding the role of the polymer matrix on the post-processing segregation. Films of elastomeric matrices like the copolymer of Styrene-*b*-ethylene-butylene-*b*-styrene (SEBS) presented enhanced segregation of surface modifying molecules[24], but no study investigating this effect over time in electrospun mats has been reported so far.

This work aims to understand the morphology evolution of electrospun SEBS blends using both PEO-PPO-PEO and pure PEO as surface modifying polymers. The surface energy and architecture of each molecule are used to explain the final surface morphology, composition and wettability right after electrospinning and after ageing at room temperature. A comparison between SEBS and pure PS in respect to their ability to allow segregation is also presented.

MATERIALS AND METHODS

Thermoplastic elastomer SEBS (grade G1652, $M_w = 79\,000\text{ g}\cdot\text{mol}^{-1}$) with 30 wt% of Styrene (S) blocks was kindly supplied by Kraton. Pure polystyrene (PS, $M_w = 238\,000\text{ g}\cdot\text{mol}^{-1}$), two types of amphiphilic PEO-PPO-PEO, F127 ($M_w=12\,600\text{ g}\cdot\text{mol}^{-1}$) with 73.2 wt% of EO blocks and P123 ($M_w = 5\,800\text{ g}\cdot\text{mol}^{-1}$) with 30 wt% of EO blocks, and pure PEO ($M_w = 12\,000\text{ g}\cdot\text{mol}^{-1}$) were purchased from Sigma Aldrich. Toluene and Chloroform were purchased from Fisher Scientific.

Solutions with a total polymer concentration of 15 wt% were prepared by dissolving the weighed polymers together in Chloroform/toluene (80/20 wt%) using a magnetic stirrer. The

solutions were extracted from the beakers with syringes connected with 14G needles that were later changed to 21G needles used for the electrospinning process. The flow rate of $2\text{mL}\cdot\text{h}^{-1}$ during electrospinning was controlled with a syringe pump (PHD Ultra, Harvard Apparatus) and the voltage applied to the needle, 15 kV, was controlled by a high voltage power supply (SL40*150, Spellman). A grounded flat collector was placed 15 cm from the needle. Blends of SEBS with either pure PEO or PEO-PPO-PEO (F127 and P123) were prepared and named as PEO_ x , F127_ x or P123_ x , where x is the amount of each polymer (5, 10, 15 and 20 wt%) in the blends after solvent evaporation. Higher contents of these polymers caused process disruption due to their relative low molecular weight. Later, blends with PS as the matrix were prepared using the same parameters with the exception of the flow rate, which was set at $1\text{ mL}\cdot\text{h}^{-1}$, and total polymer concentration at 20 wt%. Additionally, glass slides were dip-coated in the solutions of pure polymers using a dip-coater (Dip-Master 50, Chemat Technology) with a residence time of 3 seconds and speed of $10\text{ mm}\cdot\text{min}^{-1}$ to prepare flat films for the surface energy analysis.

After electrospinning, several $1\times 1\text{ cm}$ samples were prepared and kept sealed at room temperature for the surface chemical compositions analysis over time. X-ray photoelectron spectroscopy (XPS) was performed to analyse the first 10 nm of the fibers surface using an ESCALAB 3 MKII with a Mg $K\alpha$ source and 216W (12 kV, 18 mA) of power. The mat area analysed in each sample was $2\times 3\text{ mm}$ and so the result is an average of all fibers present in this area. Repeated tests with selected SEBS/PEO-PPO-PEO compositions revealed a variation of approximately 5%.

Contact angle measurements were performed with a goniometer (VCA Optima, AST products Inc.) and ultrapure water (Milli-Q[®]) to verify if the electrospun mats were hydrophobic or hydrophilic (absorbing). The contact angles of both formamide and diiodomethane on flat films

of the pure polymers were measured for the surface energy calculation using the Owens-Wendt method [25, 26].

Scanning electron microscopy (SEM) was performed to observe both the mat and fiber surface morphology using a SU-8230 microscope (Hitachi) at 5kV in secondary electrons mode. The samples were coated with platinum (Q150T S sputter coater, Quorum Technologies).

RESULTS AND DISCUSSION

Figure 1 shows the mat morphology of electrospun pure SEBS (Figure 1a) and the blends containing the highest concentration (20 wt%) of F127 (Figure 1b), P123 (Figure 1c) and pure PEO (Figure 1d). Pure SEBS presented uniform fibers with diameter around 11 μm . The incorporation of each one of the additives helped to reduce the final diameter possibly due to changes in the rheological and electrical properties of the solution. It is known that a decrease in viscosity[27] or an increase in the dielectric constant of the solution[28] can facilitate the thinning of the jet during electrospinning and produce fibers with smaller diameter. F127_20, P123_20 and PEO_20 mats were composed of fibers with an average diameter of around 5, 7, and 6 μm , respectively. The presence of 20 wt% of P123, the smallest molecule used in this study ($M_w = 5\,800\text{ g}\cdot\text{mol}^{-1}$), in the solution caused some disruption during electrospinning, producing more fibers with nonuniform diameter and merging contact points. The mats of pure SEBS and PEO_20 were hydrophobic and presented similar high values of static contact angle (Figure 1a and 1d), while the mats of F127_20 and P123_20 (Figure 1b and 1c) were superhydrophilic and absorbed the water droplet.

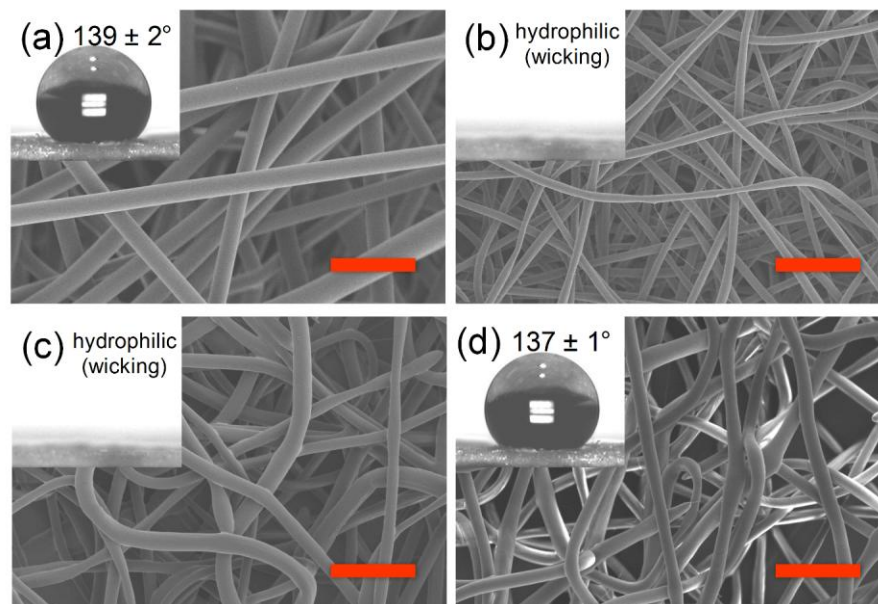


Figure 1 – Mat morphology and static contact angle results for (a) pure SEBS, (b) F127_20, (c) P123_20 and (d) PEO_20. Scale bars = 50 μ m.

Figure 2 shows the surface chemical composition results obtained by XPS. To allow complete solvent evaporation, the measurements were made 24 hours after electrospinning. The oxygen concentration, calculated from the areas of the photoemission peaks of C 1s and O 1s in the XPS survey spectrum (Figure 2a), was used as an indicator of PEO or PEO-PPO-PEO presence at the surface, considering that there is no oxygen in the SEBS matrix (Figure 2a). This atomic concentration was then converted to PEO or PEO-PPO-PEO concentration (as shown in Figure 2b) using the theoretical carbon to oxygen (C:O) ratio in each of the pure chemical structures (PEO, F127 or P123). Results of XPS surveys performed on films of the pure polymers revealed good agreement with this theoretical oxygen concentration. The horizontal arrow in Figure 2b indicates an estimated transition point above which all the mats were hydrophilic and started to absorb water (onset of wicking based on surface chemical composition). All mats below the

arrow were hydrophobic and presented high values of water contact angle similar to pure SEBS mats ($\approx 140^\circ$).

SEBS/P123 blends presented the greatest level of PEO-PPO-PEO segregation to the surface, way above the blend bulk composition line, reaching complete hydrophilization at 10 wt% of P123 and almost surface saturation at 20 wt%. Blends with F127 also presented surface enrichment for all compositions due to the segregation of PEO-PPO-PEO, but the onset of wicking was achieved only at 20 wt% of F127. Pure PEO was much less effective to modify the surface of SEBS fibers and the analysis showed PEO depletion up until 15 wt% of PEO in the SEBS/PEO blends, and hydrophobicity for all the SEBS/PEO mats.

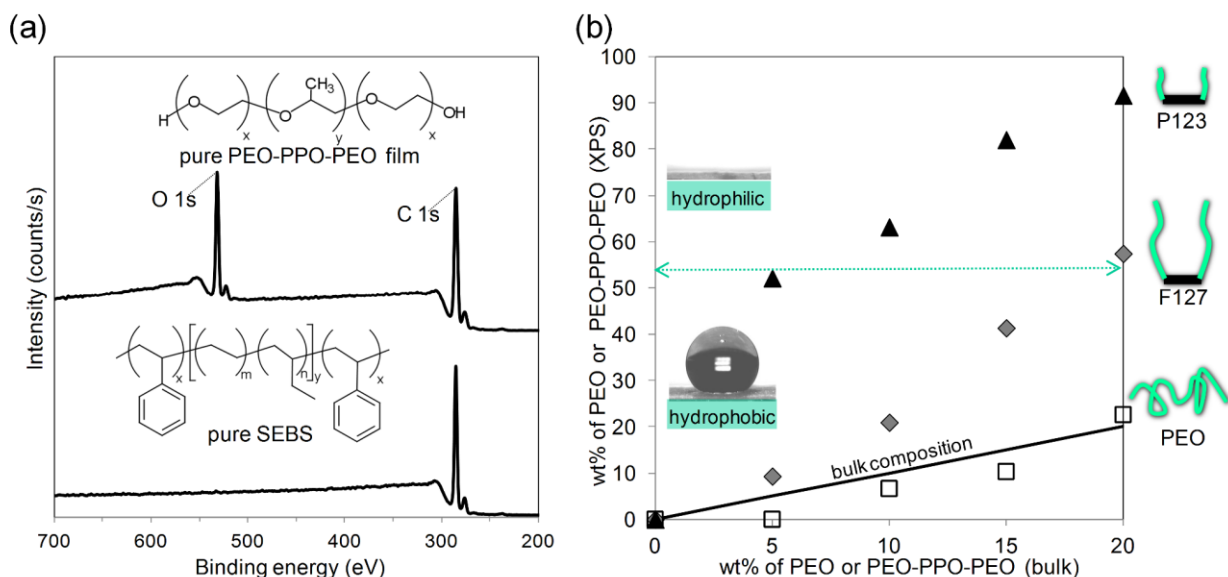


Figure 2 – XPS results: (a) Survey spectra for pure PEO-PPO-PEO and pure SEBS showing the photoemission peaks of C 1s and O 1s. (a) Surface chemical composition of SEBS/PEO-

PPO-PEO (grey diamonds for SEBS/F127, black triangles for SEBS/P123) or SEBS/PEO (open squares) blends after processing (day 1) as a function of PEO-PPO-PEO (F127 or P123) or PEO concentration (0, 5, 10, 15 and 20 wt%).

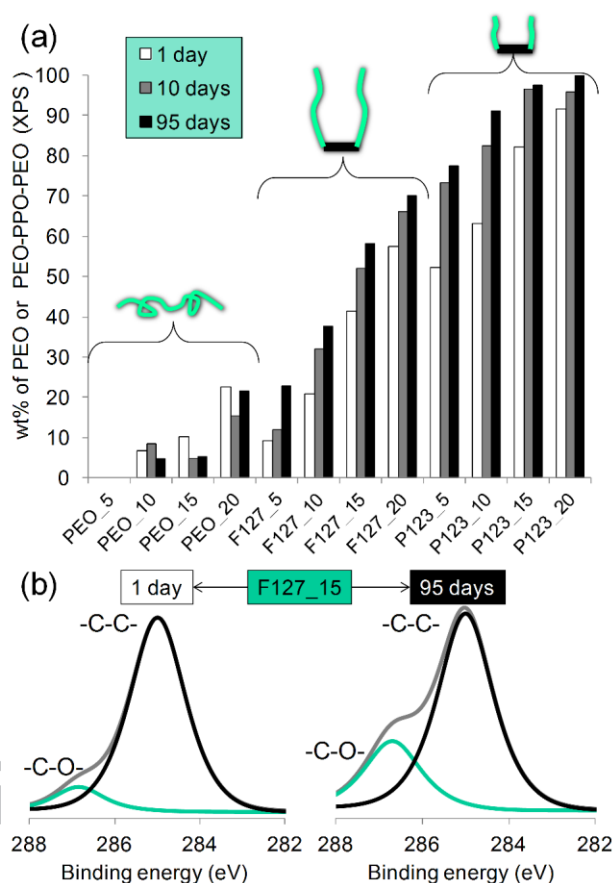


Figure 3 – XPS ageing results: (a) Survey results showing PEO or PEO-PPO-PEO (F127 or P123) segregation to the surface over time in the SEBS-based blends; (b) High-resolution spectra showing intensity increase in the $-C-O-$ peak over time.

One day after the electrospinning process the mat of the blend with 5 wt% of P123 (P123_5) was hydrophobic. Blends with higher PEO-PPO-PEO content at the surface were completely superhydrophilic while the ones with lower PEO-PPO-PEO surface concentration were

completely hydrophobic (Figure 2b). However, days after processing, new water contact angle measurements revealed that the P123_5 mat became hydrophilic with fast water absorption. Similarly, the F127_15 mat that was hydrophobic right after processing also became hydrophilic, although the droplet absorption time varied greatly depending on the mat region[13]. These results led to the investigation presented in Figure 3a that shows the evolution of the surface chemical composition of the mats over time after storage in a sealed package at room temperature (22-23 °C). Surface enrichment by segregation continued even after total solidification. The blends SEBS/P123, in particular, showed a sharp segregation in the first 10 days after processing followed by a slight increase/stabilization in the next months. After ageing, P123_15 and P123_20 presented a P123 wt% very close to the theoretical value obtained for pure P123 molecules, which reinforces the hypothesis of P123 migration and indicates a complete surface coverage with PEO-PPO-PEO. SEBS/F127 blends also presented continued, although less sharp, segregation but stabilized at lower values never reaching complete coverage. High resolution XPS (Figure 3b) in both as processed (1 day after) and aged samples revealed that the increase in oxygen content at the surface was due to the greater presence of -C-O- bonds, which exists in both PEO and PPO blocks, and that no chemical reaction occurred. In the case of SEBS/PEO blends there was no clear trend of continued segregation and some of the blends even presented a lower value of PEO at the surface after 95 days. All the SEBS/PEO mats remained hydrophobic even after ageing.

Considering that both PEO and PEO-PPO-PEO are immiscible with SEBS (observed by optical microscopy of films and Differential Scanning Calorimetry, not shown here), an attempt to predict the equilibrium morphology of the blends was made with surface tension measurements and interfacial tension calculations to understand the segregation results. The

Owens-Wendt method was used to calculate the surface tension of pure SEBS, PS, PEO-PPO-PEO (F127) and PEO films. Formamide was used as the polar test liquid while diiodomethane was the nonpolar test liquid[25, 26, 29]. Contact angle measurements with the liquid pair were performed on the surfaces of flat films of each pure polymer, obtained by dip-coating. The results enabled the surface tension calculation as the sum of dispersion and polar components (Table 1).

Table 1 – Surface tension values calculated by the Owens-Wendt method, and taken from literature as indicated.

polymer	surface tension (mN/m)		
	γ^d	γ^p	γ
SEBS	35.7	2.1	37.8
PS	41.4	0.2	41.6
PEO-PPO-PEO	45.7	0.0	45.7
PEO	44.6	3.8	48.4
PEO ¹	30.7	12.2	42.9
PPO ¹	31.3	0.4	31.7

¹Values taken from ref[30]

The harmonic mean equation

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$

was used to calculate the interfacial tension γ_{12} between the polymers *I* (SEBS or PS) and 2 (PEO, PEO-PPO-PEO or PPO), where γ_i^d and γ_i^p are the dispersion and polar components of the surface tension γ_i , which can also be interpreted as the interfacial tension between polymer *i* and

air. The interfacial tension values were then used to calculate the three spreading coefficients presented in Figure 4 with the possible surface morphologies[15, 16]. The results are summarized in Table 2.





		spreading coefficients		
		$\gamma_2 - (\gamma_{12} + \gamma_1)$	$\gamma_{12} - (\gamma_1 + \gamma_2)$	$\gamma_1 - (\gamma_{12} + \gamma_2)$
(i)		> 0	< 0	< 0
(ii)		< 0	< 0	< 0
(iii)		< 0	< 0	> 0
(iv)		< 0	> 0	< 0

Figure 4 – Possible blend surface morphologies according to surface and interfacial tension values and spreading coefficients. Polymer 1 (orange) is the SEBS or PS matrix and polymer 2 (green) represents either PEO or PEO-PPO-PEO.

Table 2 – Interfacial tension, spreading coefficients and possible morphologies for the polymer blends using either hydrophilic PEO or amphiphilic PEO-PPO-PEO as surface modifying polymers in a SEBS or PS matrix.

	γ_{12} (mN/m)	$\gamma_2 - (\gamma_{12} + \gamma_1)$	$\gamma_{12} - (\gamma_1 + \gamma_2)$	$\gamma_1 - (\gamma_{12} + \gamma_2)$	Morphology (Fig 4)
SEBS/PEO	1.5	> 0	< 0	< 0	(i)
SEBS/PEO-PPO-PEO	3,3	> 0	< 0	< 0	(i)
SEBS/PEO ¹	7.4	< 0	< 0	< 0	(ii)
SEBS/PPO ¹	1.5	< 0	< 0	> 0	(iii)
PS/PEO	3.4	> 0	< 0	< 0	(i)
PS/PEO-PPO-PEO	0.4	> 0	< 0	< 0	(i)
PS/PEO ¹	13.2	< 0	< 0	< 0	(ii)

PS/PPO ¹	1.5	< 0	< 0	> 0	(iii)
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¹Calculated with the values found in literature (see Table 1)

The interfacial tension values calculated from the surface tension measurements for pure SEBS, PEO and PEO-PPO-PEO (F127) reveal that for all blends the equilibrium morphology would be the case (i) presented in Figure 4, with the dispersed phase droplet of polymer 2 (PEO or PEO-PPO-PEO) inside the polymer 1 (SEBS) matrix. The morphology would not change if SEBS was replaced by pure PS. At first, this analysis leads to the conclusion that if the thermodynamic equilibrium was reached the morphology evolution would result in less PEO or PEO-PPO-PEO at the surface, contrary to what was observed in the ageing experiments. In fact, Figure 3 shows an increase of PEO-PPO-PEO at the surface leading to surface saturation for some compositions. Some factors can contribute to the lack of precision involved in the method chosen for the surface tension calculation. Block copolymers films may present a degree of surface roughness that can alter the contact angle results. Also, films of PEO or PEO-PPO-PEO (F127) are soluble or leachable when in contact with different liquids like water, formamide and diiodomethane. The contact angle was taken instantly after the droplet deposition, but this probably contributed to increase the measurement error. Moreover, the amphiphilic polymer with smaller molecular weight (P123) did not form a film without cracks and was left out of this analysis. But most importantly, this method does not permit to separate the values of hydrophilic PEO and hydrophobic PPO blocks, giving only an average value that does not correspond to the behavior of each block. In order to circumvent these uncertainties, the interfacial tension was also calculated using separate surface tension values for PEO and PPO found in literature (Table 1) that were obtained by different methods[30] to avoid contact with solvents, such as the pendant drop[31] with the pure molten polymers (PEO or PPO) and extrapolation to room temperature. By recalculating the spreading coefficients for SEBS and pure PEO the new

morphology obtained corresponds to the case (ii) in Figure 4 with the PEO droplet reaching the air surface while still inside the matrix. The new spreading coefficients for SEBS and pure PPO leads to the morphology (iii) in Figure 4, with a wetting layer of PPO separating the SEBS matrix from the air.

These new equilibrium morphologies help to explain the remarkable segregation and the evolution towards surface enrichment and saturation in the SEBS/PEO-PPO-PEO blends. As previously proposed, the low surface energy PPO block drives the segregation of the amphiphilic PEO-PPO-PEO to the surface[13, 18]. Pure PEO and F127 have a similar molecular weight but the segregation is much more effective with the amphiphilic polymer. The size of the molecule and the PPO/PEO ratio influence the level of PEO-PPO-PEO segregation. F127 and P123 have similar PPO block size but P123 has shorter PEO chain-ends and therefore lower molecular weight, resulting in a more drastic segregation and even surface saturation. Any segregation of higher energy molecules to the surface may be explained by the difference in molecular weight between the modifying polymer and the matrix. As previously reported, two factors may be responsible for this effect: (i) chain ends present lower surface energy than the main chain so that polymers with lower M_w have greater tendency to segregate to the surface; (ii) a decrease in M_w leads to a decrease in the conformational entropy penalty for a polymer chain located at the surface so that the enthalpic/energy effects may be overcome[21]. Combining both enthalpic (low surface energy) and entropic (low molecular weight) will then lead to a greater segregation, like it was observed for the blends containing P123 ($M_w = 5\ 800\ \text{g}\cdot\text{mol}^{-1}$) molecules.

Nevertheless, it is still unclear if the fiber surface is covered only by phase-separated PEO-PPO-PEO polymer or if free amphiphilic molecules also contributed to the surface coverage. PEO-PPO-PEO presents surfactant properties, meaning that in aqueous solutions free amphiphilic molecules tend to segregate to the surface and form a layer until the surface is

saturated. By increasing the surfactant concentration micelles start to form and aggregate inside the solution leading to observable phase separation. The surface saturation is followed by a decrease in surface tension and in the case of PEO-PPO-PEO copolymers, the PPO block will cover the surface with air while the PEO is immersed in the solution. In a solution containing polymers, the surfactant molecules still form this type of layer even though the interaction with polymer chains makes the segregation more difficult[32, 33]. Surface tension values for PEO-PPO-PEO copolymers are usually measured in solution due to this ability to form a layer, and the values reported[34] are close to the ones presented in Table 1 for pure PPO, confirming that in aqueous solutions the PPO block covers the surface while the PEO block stays in the aqueous phase. The values in Table 1 also show that PPO presents the lowest surface tension value in the blends, while PEO presents the highest value.

To observe the morphology by SEM, the blends with the highest amount of either PEO-PPO-PEO or PEO were washed and immersed in water for 24h. After that, the procedure was repeated five more times in order to extract PEO-PPO-PEO or PEO. Figure 5 shows the edge of a mat and a cross-section of a fiber of PEO_20 (Figure 5a and 5b) and P123_20 (Figure 5c and 5d). PEO_20 mats presented more homogeneous fibers (Figure 5a) while P123_20 fibers presented greater variation in diameter and shape (Figure 5c). It is possible to observe some holes in the lateral surface that may indicate phase-separated PEO extracted from PEO_20 (Figure 5b). The cross-section revealed elongated droplets (indicated by the arrow) but it is not clear if this indicates PEO extraction or just surface roughness. Due to the lower presence of PEO at the fibers surface, the extraction did not completely reveal the morphology of PEO_20 blends (Figure 5b). In the case of F127_20 a different type of morphology formed a phase-separated structure that contributed to the homogeneous wetting behavior, as previously discussed in more detail in ref[12]. The cross-section of P123_20 fibers (Figure 5d) clearly showed the phase

separation between the polymers after P123 extraction. The lateral surface of the fiber in Figure 5d shows that, different from blends with pure PEO, larger regions were covered by phase-separated P123, leaving a rougher surface after extraction. From the XPS results it was found that this composition presented saturated surface even before ageing.

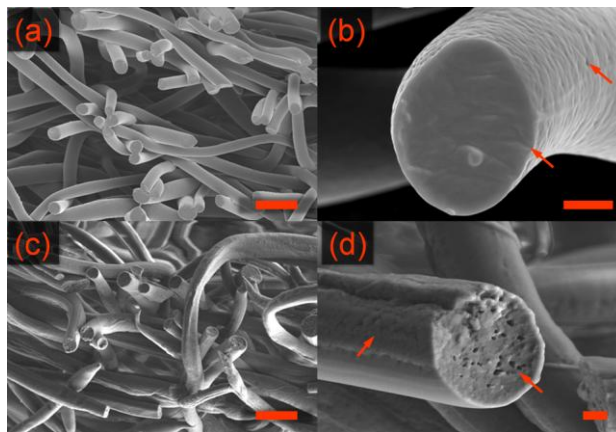


Figure 5 – Edge of a cut mat and cross section of a fiber after washing: (a) and (b) PEO_20; (c) and (d) P123_20. Scale bars = 20 μm in (a) and (c); 2 μm in (b) and (d).

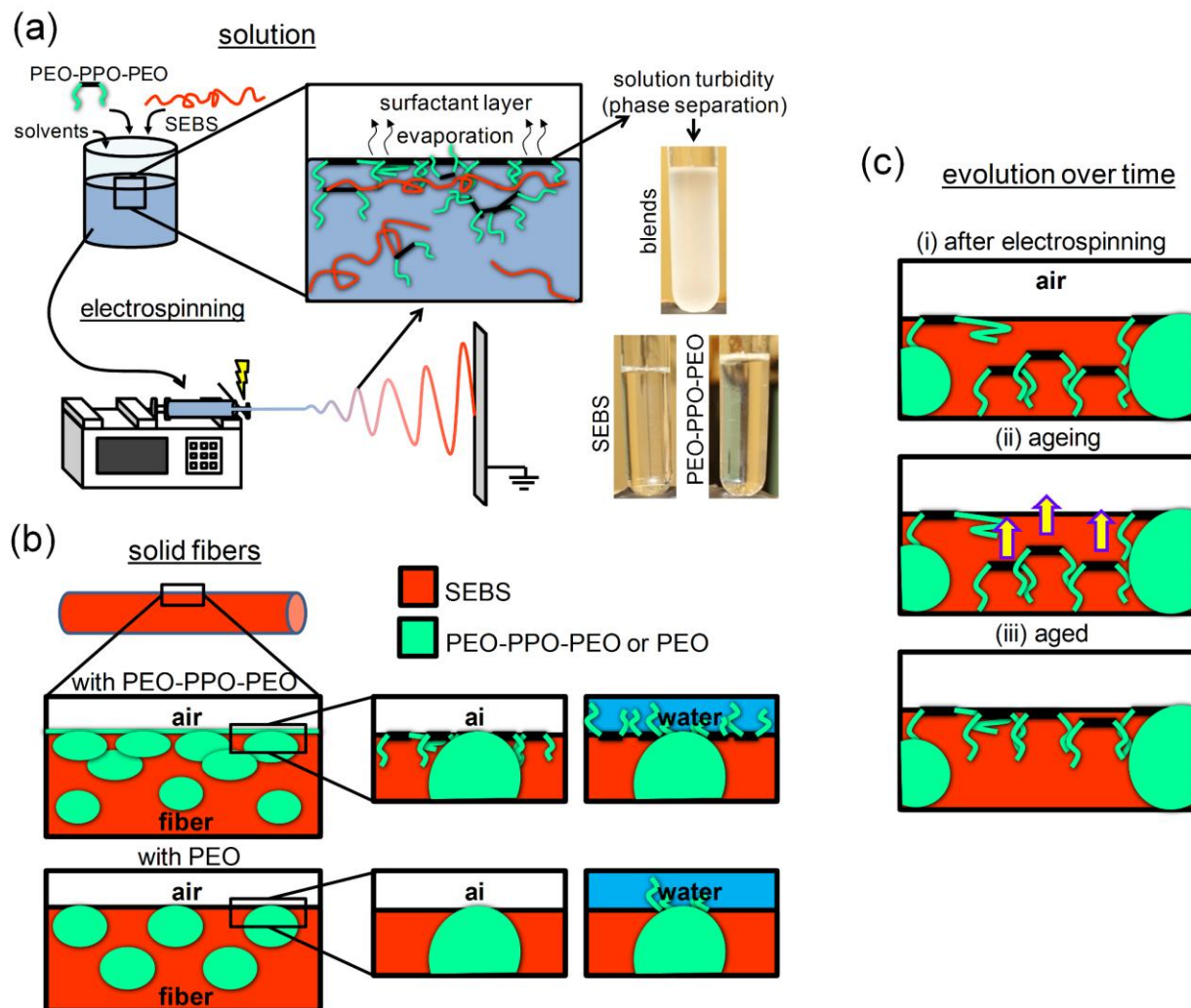


Figure 6 – Schematic illustrations: (a) solutions containing SEBS and PEO-PPO-PEO with pictures of representative solutions; (b) surface enrichment and hydrophilization mechanism with amphiphilic PEO-PPO-PEO or pure PEO (out of scale); (c) Ageing mechanism showing PEO-PPO-PEO molecules that continue to segregate to the surface over time after solidification.

The clear phase separation (SEM) and surface coverage (XPS) indicate that in the blends with amphiphilic copolymers the morphology evolved as presented in the attempted mechanisms in Figure 6. As previously explained, with the evaporation of the organic solvents PEO-PPO-PEO molecules tend to segregate to the polymer-rich solution surface (Figure 6a). Inside the solution,

the amphiphilic molecules start to interact with SEBS chains and also form micelles, leading to phase-separated structures. The turbidity of the solutions containing both polymers is a clear indication of large phase-separated agglomerates, while the solutions of both pure SEBS and pure PEO-PPO-PEO are transparent (Figure 6a). After electrospinning (Figure 6b), the chemical composition of the fiber surface is defined by both this original layer of amphiphilic molecules and also by phase-separated structures that reached the surface, which makes blending with amphiphilic molecules much more effective to hydrophilize the mat. Besides greater surface energy, pure PEO does not have surfactant properties and the main contribution to the surface modification of SEBS/PEO blends comes from phase-separated structures that reached the surface, which was not enough to produce hydrophilic mats.

The fiber surface morphology evolution can be divided in three stages (Figure 6c). During electrospinning the surfactant layer of the solutions may be disrupted by the rapid jet bending and fiber solidification, “freezing” the microstructure in the after-processing morphology and chemical composition (Figure 6c (i)) and, as shown in XPS results, the resulting fiber surface presented great enrichment, although without completely coverage. Molecules close to but not at the surface right after electrospinning continued to move to the surface with time (Figure 6c (ii)) and formed the aged morphology (Figure 6c (iii)) with increased segregation. In addition, it is much more unlikely that larger, phase-separated structures would be able to move in the solid state.

Another factor that influences the segregation is the mobility of the surface modifying molecules, which depends on the matrix free volume fraction. It is known that annealing of polymer blends above the glass transition temperature of the matrix increases the mobility of the

polymers and allows surface modification[4, 23, 35]. The free volume fraction f of an amorphous polymer at a given temperature T can be estimated by the expression[36]

$$f = f_g + \alpha_2(T - T_g)$$

where f_g is the fraction of free volume at the glass transition temperature T_g , and α_2 is the difference between the thermal expansion coefficient above and below the glass transition temperature. As obtained by the Williams–Landel–Ferry equation[36], $f_g = 0.025$ and $\alpha_2 = 4.8 \times 10^{-4} \text{ K}^{-1}$, and considering that the overall glass transition temperature of SEBS is -42°C due to the presence of 70 wt% of elastomeric EB blocks, $T - T_g \approx 65 \text{ K}$. In these conditions, the free volume fraction f would more than double the f_g value, facilitating the segregation of other molecules to their equilibrium state without the need for annealing at higher temperatures. To verify this hypothesis, blends containing the same amount of P123, which presented marked segregation over time (Figure 3), were prepared using either SEBS or pure PS ($T_g = 100^\circ\text{C}$) as matrices. The results presented in Figure 7 show practically no sign of ageing in the PS/P123 samples. The rigidity and lower free volume fraction of the matrix prevented further movement and the structure obtained after electrospinning is preserved over time.

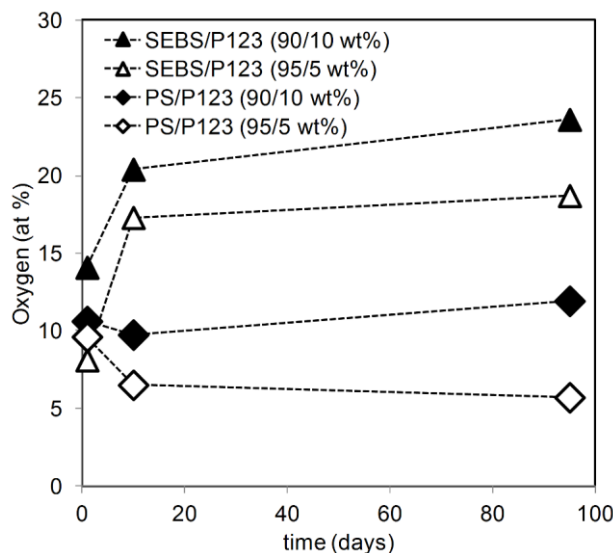


Figure 7 – Evolution in oxygen content over time for the blends containing 5 and 10 wt% of P123 in SEBS or PS matrix.

CONCLUSIONS

This work investigated polymer blending with hydrophilic or amphiphilic molecules as a technique to hydrophilize the surface of hydrophobic SEBS electrospun mats. After processing, blends with amphiphilic PEO-PPO-PEO (F127 or P123) copolymers presented a drastic PEO-PPO-PEO segregation to the surface and mat hydrophilization, while the SEBS/PEO mats were all hydrophobic. P123, the block copolymer with shorter PEO chain-ends and lower molecular weight, segregated more than F127. SEBS/PEO mats revealed depletion of PEO at the surface up until 15 wt% of PEO, and mild enrichment in the blend with 20 wt% of PEO.

Contact angle measurements on some of the mats (P123_5 and F127_15) revealed a change in wetting behavior over time at room temperature. A systematic analysis of the surface chemical composition revealed that the segregation of amphiphilic molecules continued over time, stabilizing only after weeks. In the blends with higher P123 content the fiber surface practically presented complete coverage. This continued morphology evolution is due to the movement of

amphiphilic molecules that tend to move to the surface to decrease the total energy of the system, forming a layer of PPO blocks. Mild segregation of PEO probably happened due to entropic factors.

Segregation also seems to be influenced by the mobility (free volume fraction) inside the matrix. Flexible SEBS-based (glass transition temperature around -42°C) blends presented greater segregation than rigid PS-based (glass transition temperature around 100°C) blends.

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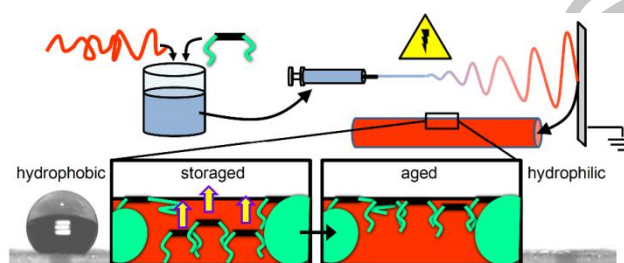
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Surface properties evolution in electrospun polymer blends by
segregation of hydrophilic or amphiphilic molecules

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Highlights

- Amphiphilic PEO-PPO-PPO segregates more to the fibers surface than hydrophilic PEO;
- Hydrophilization of electrospun mats can be achieved with low PEO-PPO-PPO content;
- Surface energy contributes to the continuing segregation of amphiphilic molecules;
- The polymer matrix is critical in allowing surface segregation at room temperature.

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