Aniline tetramer embedded polyurethane/siloxane membranes and their corresponding nanosilver composites as intelligent wound dressing materials

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Supplementary information

S1. Schemes, Figures and Table



Scheme S1: Synthetic route to polyurethane/siloxane networks

FTIR spectrum of Si-PU (Figure S1) showed a broad band centred at 3335 cm⁻¹, which was attributed to the stretching vibration of urethane and urea N-H groups. The urethane carbonyl (NH-CO-O-) group was detected as a strong peak at 1716 cm⁻¹. The peak observed at 1545 cm⁻¹ was attributed to C-N stretching, combined with N-H out-of-the-plane bending of urethane groups, and the stretching vibration of ether (C-O-C) groups was noticed as a peak at 1100 cm⁻¹. The presence of methoxysilane (-Si-O-CH₃) and urea carbonyl (-NH-CO-NH-) peaks at their corresponding absorptions of 950 cm⁻¹ and 1675 cm⁻¹, and the absence of NCO groups peak at 2230 cm⁻¹ indicated the complete reaction of isocyanate and NH₂ groups.



Figure S1: FTIR spectrum of Si-PU

FTIR spectrum of AT (Figure S2a) showed peaks at 3340 and 3185 cm⁻¹ associated to amine groups. Stretching vibrations of quinoid and benzenoid rings were also appeared as peaks at 1591 and 1495 cm⁻¹, respectively. After reaction with coupling agent (Figure S2b) the peaks related to terminal amine were diminished considerably and two new peaks at 1653 and 1701 cm⁻¹ were appeared, which related to the formation of the imine (-N=CH-) and aldehyde (-CHO) groups, respectively. After reaction of GA-AT with APS, the peak of free aldehyde groups disappeared, but the peak of imine moiety at 1659 cm⁻¹ was intensified (Figure S2c).



Figure S2: FTIR spectrum of (a) AT, (b) GA-AT, and (c) Si-AT

The strong band observed at around 300 nm was attributed to π - π * transition of the benzene rings. The weak and broad band appeared in the range of 550-680 nm is related to the benzenoid (B) to quinoid (Q) π_B - π_Q excitonic transition.¹ Both GA-AT and Si-AT exhibited similar spectral pattern, despite the reaction of terminal amine group of AT molecule. Therefore, the electroactivity of these compounds was confirmed. Close inspection of Figure S3 showed lower Q/B intensity ratio for GA-AT and Si-AT than compared to AT. This phenomenon was attributed to the reduction of electronic concentration of the quinine units due to electron-withdrawing character of imine (-N=CH-) linkages.² Meanwhile, this observation confirmed the formation of GA-AT through coupling reaction of AT terminal amine group with aldehyde functionality of GA.



Figure S3: UV spectra of (a) AT, (b) GA-AT, and (c) Si-AT



Figure S4: FTIR spectrum of 9a) NEPU and (b) EAPU2



Figure S5: UV/Vis spectrum of the solution obtained from EAPU2-Ag extraction



Figure S6: Silver and silicon maps on cross-section of (a) NEPU-Ag, (b) EAPU1-Ag, (c) EAPU2-Ag, (d) EAPU3-Ag.



Figure S7: Cyclic voltammogram of EAPU2 membrane



Figure S8: Fluorescence image of stained cells on (a) TCP, (b) NEPU, (c) EAPU1, (d) EAPU2, (e) EAPU3, (f) Doped EAPU1, (g) Doped EAPU2, (h) Doped EAPU3, (i) EAPU1-Ag, (k) EAPU2-Ag, (l) EAPU3-Ag.



Figure S9: UV-vis spectra of mixtures containing (a) neat DPPH, (b) DPPH+NEPU (c) DPPH+EAPU1, (d) DPPH+EAPU2-Ag, (e) DPPH+EAPU2, (f) DPPH+EAPU3.

Table S1: Tensile properties of membranes x)

Sample	Tensile strength (Mpa)		Initial modulus (Mpa)		Elongation at break (%)	
	Dry	Wet	Dry	Wet	Dry	Wet
NEPU	5.6±0.5ª	0.3±0.1ª	0.031±0.001ª	0.011±0.001ª	107± 2 ^a	17±2ª
EAPU1	7.5±0.7 ^b	0.8±0.1 ^b	$0.048{\pm}0.001^{b}$	0.018 ± 0.002^{b}	96±3 ^b	26±3 ^b
EAPU2	10.2±1.2°	3.1±0.4°	0.114±0.015°	$0.076 \pm 0.005^{\circ}$	83±3°	47±5°
EAPU3	11.2±1.1°	3.7±0.2°	$0.431{\pm}0.025^{d}$	$0.101{\pm}0.006^{d}$	65±5 ^d	45±4°

^{x)} According to analysis of variances P-values of < 0.05 were considred significant.. The difference between quantities with similar superscripts is not significant (p ≥ 0.05) for data of each column.

Sample	E. coli	S. aureus	P.aeruginosa	C. albicans
NEPU	0	0	0	0
EAPU1	82	80	83	85
EAPU2	92	91	90	90
EAPU3	97	96	98	95
EAPU1-Ag	100	95	100	100
EAPU2-Ag	100	100	100	100
EAPU3-Ag	100	100	100	100

Table S2: Bacterial reduction percent of the prepared membranes

- 1. H. Wang, P. Guo, and Y. Han, *Macromol. Rapid Commun.*, 2006, **27**, 63–68.
- 2. B. Guo, A. Finne-Wistrand, and A.-C. Albertsson, *Biomacromolecules*, 2011, **12**, 2601–9.