Supporting Information

Reusable semi-IPN polymer networks as long-term antibacterial coatings

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Section S1: Characterization of poly (APMA-co-BMA)

Characterization

The co-polymer is characterized using Ascend NMR-500MHz (Bruker) by dissolving it in D_2O and scanned 64 times; peaks are integrated using the ^{1}H NMR spectra and the integrated peak areas are calculated. IR spectra of the co-polymer and semi-IPNs were recorded from Perkin Elmar "Spectrum Two" with range of 4000-400 cm^{-1} range in ATR mode. Molecular weight was analyzed using MALDI-TOF Autoflex Speed (Bruker).

By using ^{1}H NMR to analyze the synthesized AB polymer, its molecular weight and mole fraction of BMA are determined. Each molecule has a designated peak that can be found in the polymer structure (table 1) and represents the copolymer structure.
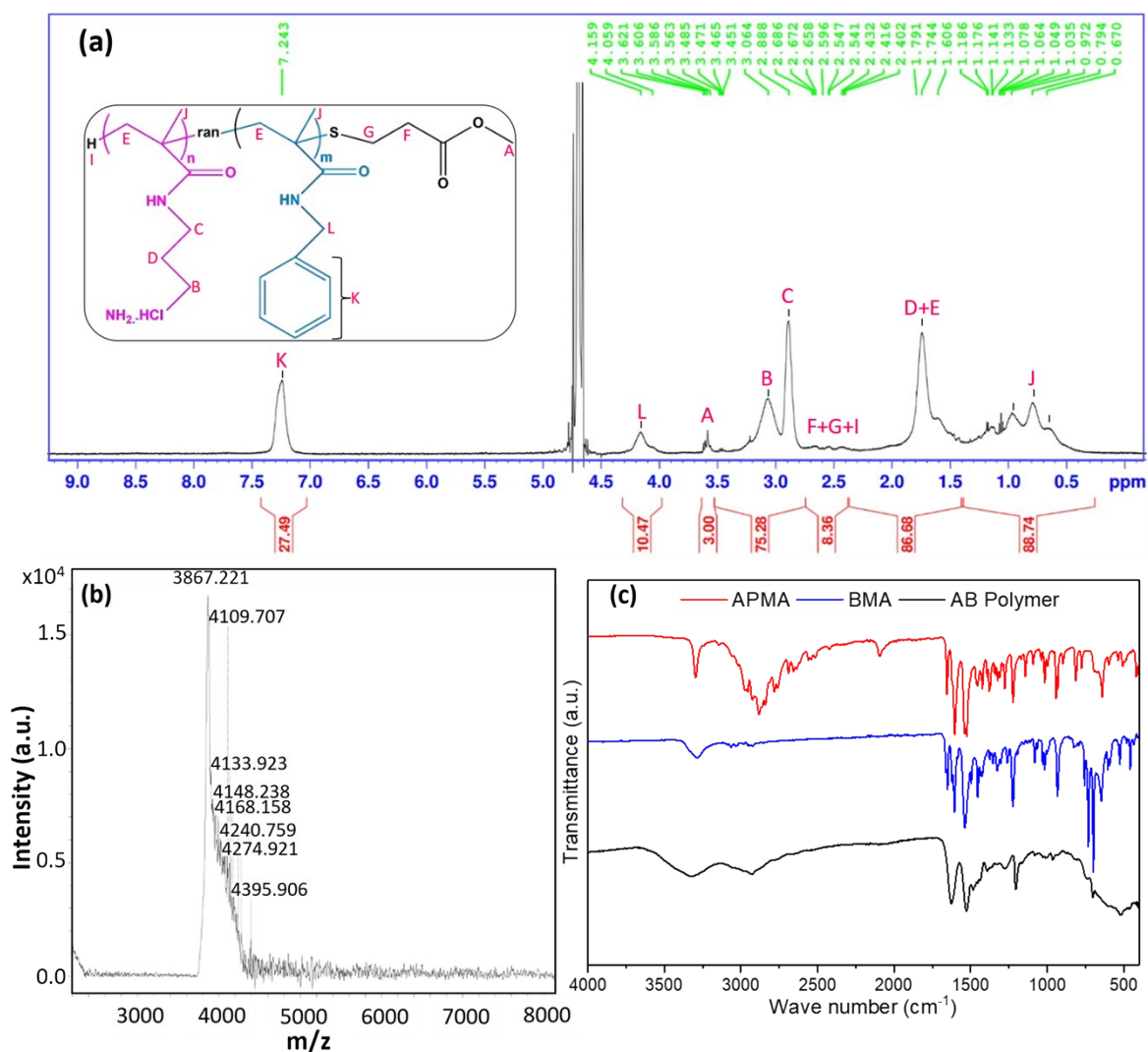
Figure S1. (a) H-NMR spectra and (b) MALDI-TOF of AB polymer. (c) ATR-FTIR transmittance spectrum of APMA, BMA and AB polymer

As shown in **figure S1a**, the spectra results revealed the chemical shifts for the end group (3.6, 2.51-2.72 ppm), BMA (7.243, 4.161, and 0.665-0.943 ppm), and APMA (1.7, 2.8-3.06 ppm). The properties of monomers and end group NMR spectra are matched by these chemical shifts.

Table S1. Peak allocated to polymer end groups and each monomer molecule discovered from NMR spectra.

Chemical Entity	Proton	Peak type	Assigned alphabet	Chemical shift (ppm)
BMA	$-C_6H_5$	Broad	K	7.24
BMA	$-CH_2$	Broad	L	4.16

End Group	CH_3COO-	Sharp	A	3.6
APMA	$-CH_2NH_3^+$ -CH2NHCO-	Broad	B+C	3.06-2.88
End Group	$-OOCCH_2CH_2SH-$	Broad multiple	F+G+I	2.68-2.4
APMA and End group	$-CH_2-$ $-SCH_2-$	Broad multiple	D+E	1.74
APMA and BMA	$-CH_3$	Broad	J	1.86-0.67

4 Protons of APMA (B+C) after integration is **75.28**. Therefore, the average number of protonated amine-functionalized repeat units per polymer chain equates to 75.28/4=**18.82** (N_{amine}).

Similarly, the peak L seen at 4.161 ppm is for methylene protons adjacent to the benzene ring. Hence the average number of methylene protons (N_{benzyl}) per individual polymer chain corresponds to 10.47/2 = **5.235**.

Degree of polymerization (DP) is the average of the total number of each monomer units' present
in an individual polymer chain, therefore, equal to

$DP = N_{amine} + N_{benzyl}$

DP= 18.82 + 5.235 = **24.055** which is rounded to a DP value of **24**.

$$f_{benzyl} = \frac{No.of\ methylene\ units\ in\ benzyl\ group}{Total\ no.of\ monomer\ units\ per\ individual\ polymer\ chain}$$

$f_{benzyl} =$ 5.235/24=0.218

Molecular weights of AMPA= 178.66 g/mol-1, BMA= 175.23
$M_n = (18.82*178.7) + (5.235*175.2)$
$= 3363.134+917.172=$**4280.306** $g\ mol^{-1}$

The molecular weight was further confirmed by analyzing the AB polymer with MALDI-TOF. **Figure S1b** displays MALDI-TOF spectra of AB polymer displaying average molecular weight of ~4200 g mol^{-1} which is closer to that of the molecular weight measured from NMR (4280.306 g mol^{-1}).

Functional groups in the monomers and AB polymer were identified using FTIR spectrum as seen in **figure S1c**. The peak at 3329 represents N-H stretching of the monomers as well as polymers. The aliphatic C-H stretching vibration (2929 cm^{-1}) in AB polymer represents the backbone of polymer chain[1]. The peak at 1655 cm^{-1} observed for APMA and BMA represents C=C stretch of both the monomers. The C=C peak is not observed in the AB polymer spectra, suggesting the conversion of monomer into polymer[2]. Since APMA and BMA are structurally similar molecules (except minor dissimilarity in pendent group), the FTIR spectra in fingerprint region are similar. An additional peak at 700 cm^{-1} for BMA which represents C-H bend for benzene ring. The characteristics peak of amide bond is seen at 1630 cm^{-1} and 1525 cm^{-1} corresponding to C=O stretch and N-H deformation[3], respectively for both monomers and polymer. Thus, the FTIR spectrum confirms the formation of the co-polymer and functional groups present.

Section S2: Contact angle and SEM evaluation of coatings after stability tests
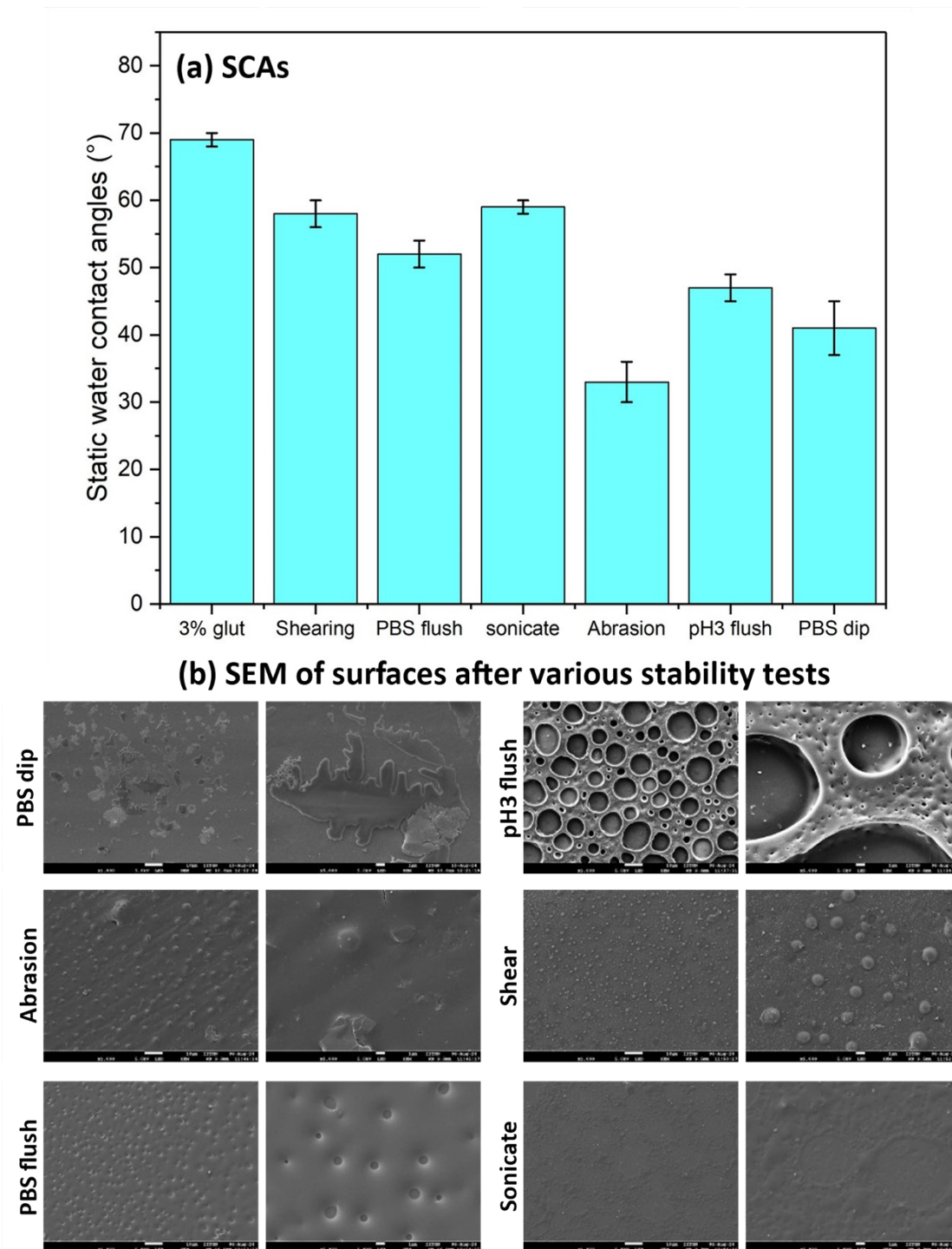

Figure S2. (a) SCAs and (b) SEM analysis of the GS-3% coatings after various stability tests

Figure S2 represents the contact angle and SEM analysis carried out after various treatments for testing durability of the coatings. SCA revealed the highest decrease in SCA for shearing action followed by PBS dip whereas, other treatments displayed similar level of drop in SCA values. SEM analysis revealed that the porosity observed in most of the coatings is due to the evaporation during drying process after drop-casting the surface.

Reference

[1] G. Pıhtılı, P. Erecevit Sönmez, F. Biryan, G. Torğut, *Polymer Engineering & Sci* **2022**, *62*, 3099.
[2] B. Dizman, M. O. Elasri, L. J. Mathias, *Macromolecules* **2006**, *39*, 5738.
[3] P. Singhsa, H. Manuspiya, R. Narain, *Polym. Chem.* **2017**, *8*, 4140.