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ELECTRONIC SUPPLEMENTARY INFORMATION

Thiol-epoxy/maleimide ternary networks as softening substrates for flexible electronics

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Experimental

Swelling

Moisture absorption was measured by weight change after immersion in phosphate buffered saline (1x PBS) solution at 37 °C at five time points over one month. Samples consisted of ~4 mg mechanically excised cylinders 3 mm in diameter and 0.5 mm in thickness. The dry mass of each sample was first measured and recorded with a Mettler Toledo ultra-microbalance with 0.1 µg precision. At each time point, samples were removed from the solution, and the surface of the polymer was gently dried using an absorbent wipe. The swollen mass was then recorded. Swelling percent was determined according to the formula:

$$q\,(\%) = {}^{(w_s - w_i)}\!/_{w_i} \times 100 \quad (1)$$

where w_s was the swollen weight and w_i was the initial, dry sample mass.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was performed using a Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer. Samples were prepared into approximately 0.5 mm thick, ~3 mm diameter cylinders. Collected spectra were then baseline-corrected using Happ-Genzel apodization. Tests were conducted under ambient atmospheric conditions. All compositions were tested at least three times.

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Swollen DMA

Swollen DMA was performed using a TA RSA-G2 with Immersion System in tension mode in order to quantify the storage modulus E' and tan δ of in phosphate buffered saline (PBS) soaked samples. All measurements

were performed on rectangular samples as having a width of 3 mm and thicknesses around 100 µm. The following parameters were selected: clamping distance of 15 mm, a preload force of 0.05 N, a frequency of 1 Hz, and a deformation amplitude of 0.275% strain. Soaking experiments were run using the immersion system of the RSA-G2 filled with PBS. The first step (the soaking) included the heating from room temperature to 37 °C followed by isothermal oscillating for 120 minutes.

Gel Fraction

Vials were prepared with approximately 10 mL of tetrahydrofuran placed in each. Three samples of each network (~ 7 mg) were weighed and then placed in a separate vial. The vials were allowed to soak for 7 days to allow all non-cross-linked material to be removed from the network polymer. The tetrahydrofuran was then removed from the vials and the samples were placed into a vacuum oven at 120 °C, 5 inHg for 24 h to drive off the remaining solvent. Finally, the polymers were equilibrated to ambient lab conditions for 24 h. The samples were then weighed again and the final polymer gel fraction was determined by subtracting the final weight from the initial weight, and normalizing to the initial weight of the sample.

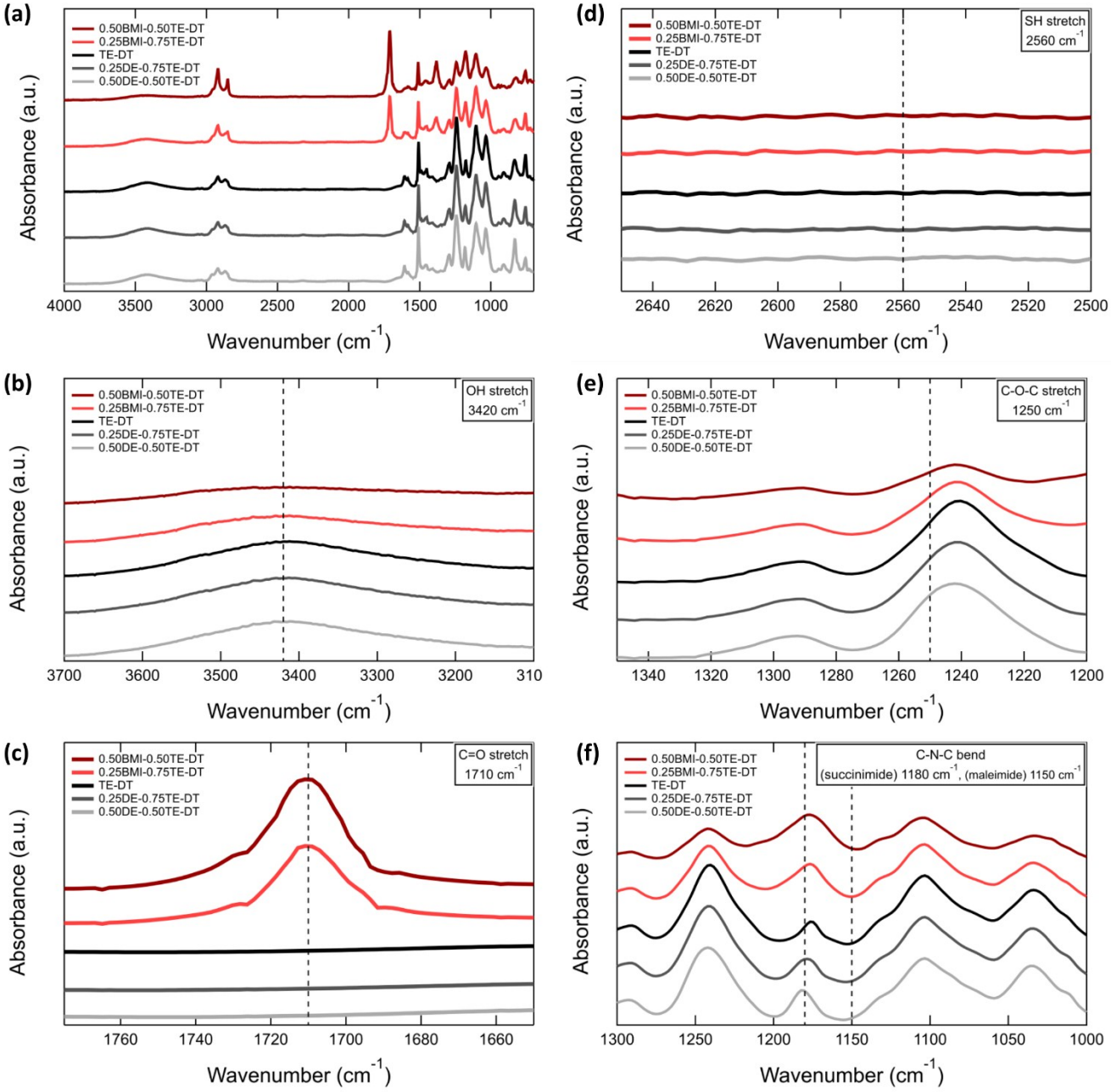

Figure S1. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra of (a) all polymer networks characterized within this work, with zoomed-in regions describing the (b) decrease in –OH and (c) increase in C=O functionality in the backbones as a function of the increasing BMI content. (d) –SH, (e) C-O-C and (f) C-N-C spectral zooms, observing the conversion of the thiol, epoxide and maleimide functionalities, respectively.

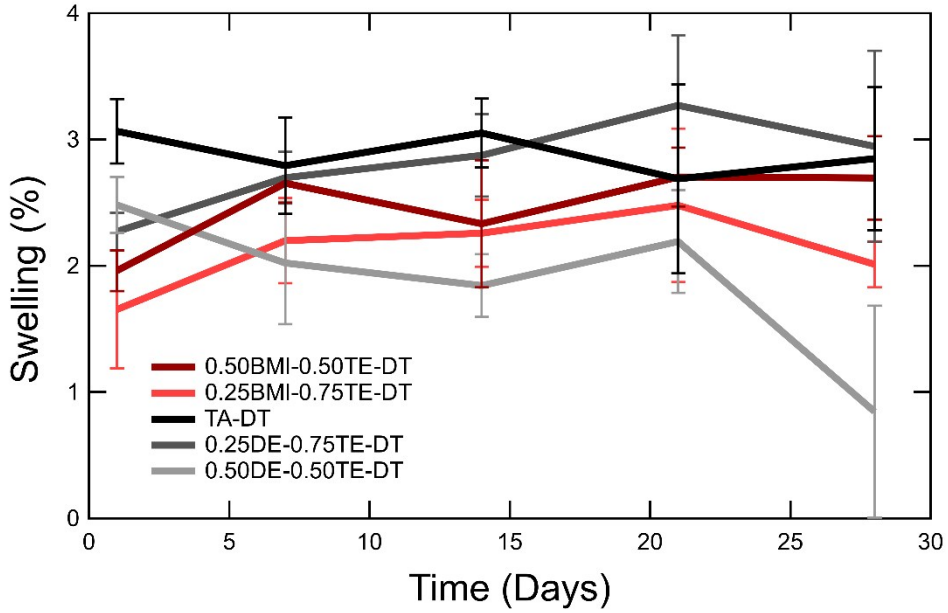

Figure S2. Summary swelling statistics for all 5 compositions tested.

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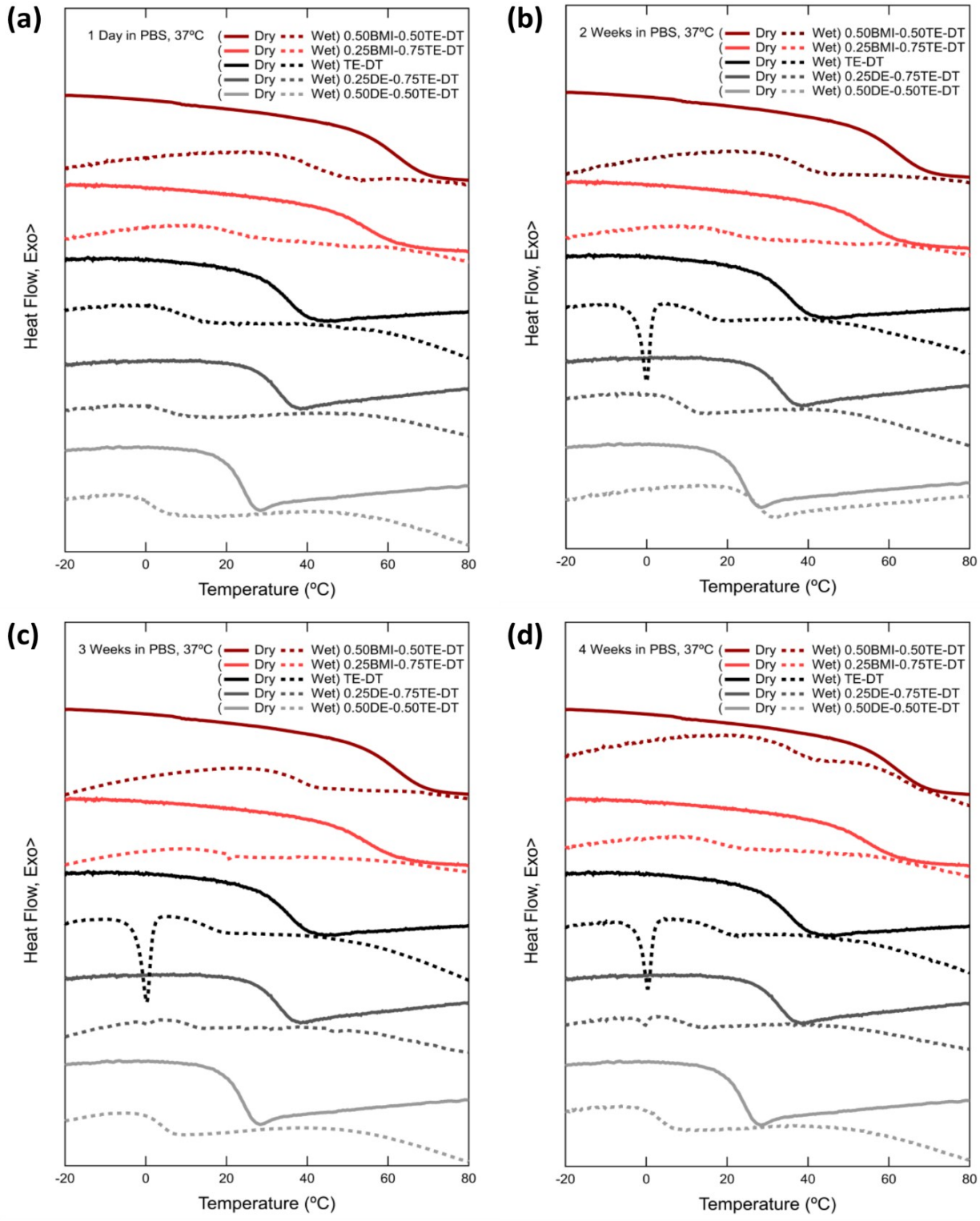

Figure S3. DSC thermograms of all five compositions tested showing dry vs. swollen behaviour over (a)1, (b) 2, (c) 3 and (d) 4 weeks.

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Thiol	Epoxy/Maleimide			Gel Fraction
DT	TE	BMI	DE	
1.00	0.50	0.50	--	0.96 ± 0.01
	0.75	0.25	--	0.95 ± 0.01
	1.00	--	--	0.97 ± 0.01
	0.75	--	0.25	0.98 ± 0.01
	0.50	--	0.50	0.98 ± 0.01

Table S1. Gel fraction statistics for all networks studied, indicating a less than 0.05 sol fraction in all compositions.

Thiol	Epoxy/Maleimide			T_g [°C]	Swollen T_g: 1 Day [°C]	Swollen T_g: 7 Days [°C]	Swollen T_g: 14 Days [°C]	Swollen T_g: 21 Days [°C]	Swollen T_g: 28 Days [°C]
DT	TE	BMI	DE						
	0.50	0.50	--	61.39 ± 1.72	40.79	36.44	36.19	35.76	35.91
	0.75	0.25	--	52.61 ± 5.74	21.61	18.69	21.53	15.28	16.88
1.00	1.00	--	--	35.46 ± 0.27	9.22	13.14	13.71	14.08	16.39
	0.75	--	0.25	32.10 ± 0.95	8.48	8.21	9.43	10.37	8.04
	0.50	--	0.50	25.11 ± 0.33	1.12	5.39	26.57[a]	4.27	2.87

Table S2. Summary statistics of all studied networks, with the monitoring of the dry versus swollen T_g over the duration of the swelling study.

[a] denotes a sample of 0.5DE-0.5TE-DT that may have dried out before the DSC run, showing a dry T_g instead of a swollen T_g.

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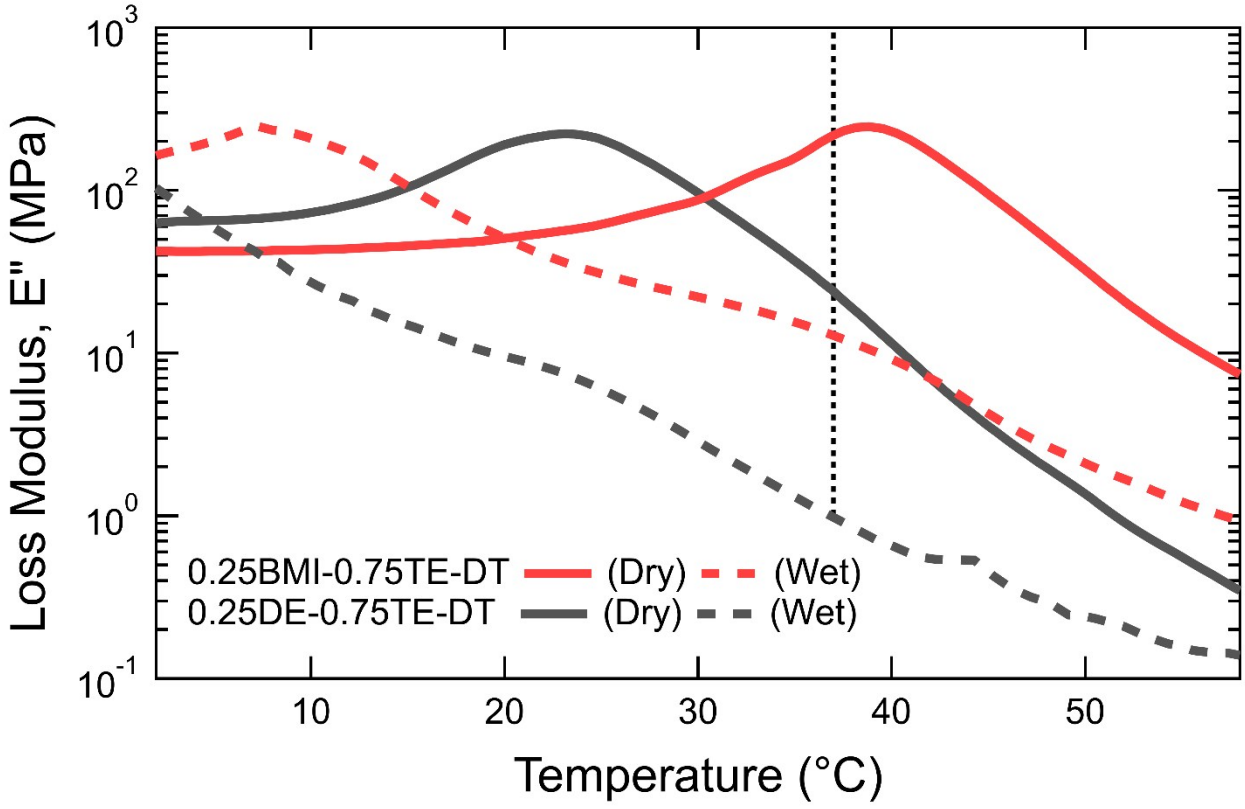

Figure S4. Dynamic mechanical analysis (DMA) of 0.25BMI-0.75TE-DT and 0.25DE-0.75TE-DT networks shows the dry and swollen (1 week, 1x PBS at 37 °C) loss modulus as a function of the temperature. The dashed gray line represents a physiological 37 °C, marking the effective modulus of these materials at that temperature.

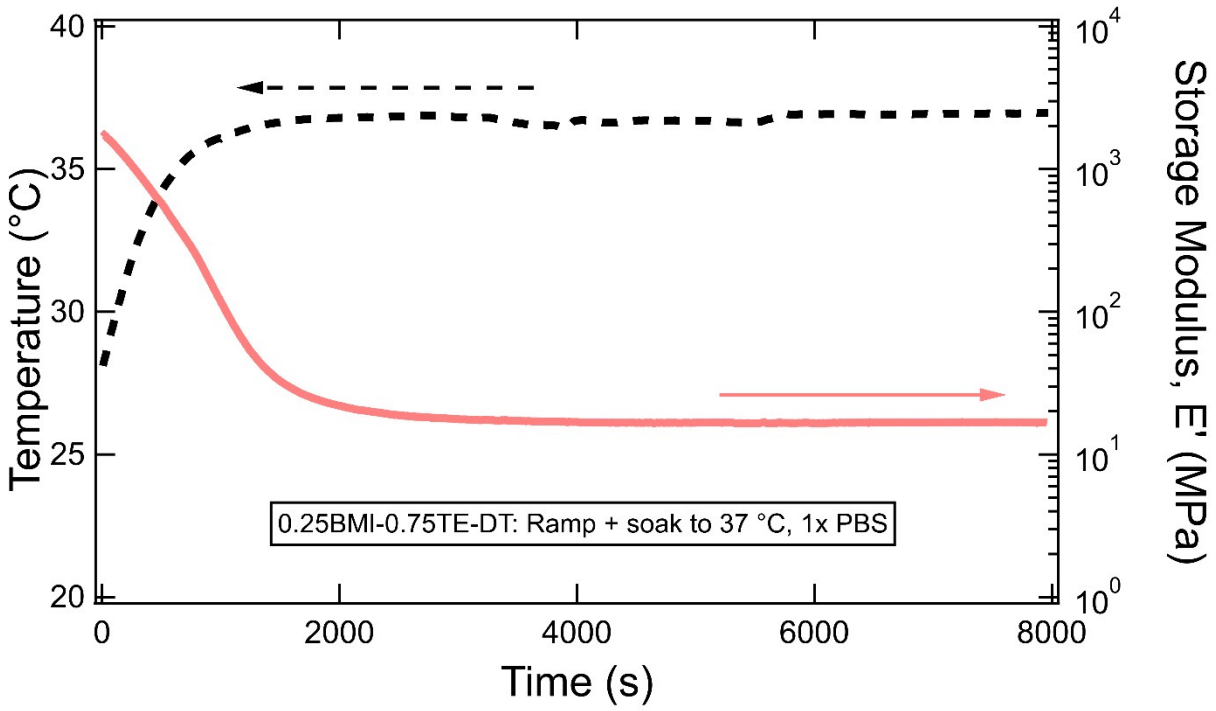

Figure S5. Isothermal soaks of 100 µm rectangular bars of 0.25BMI-0.75TE-DT, showing the storage modulus E' dynamically moving to a steady-state value of ~17 MPa after less than 1 hour soak in 1XPBS at 37 °C.