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Electronic Supplementary Information

Dynamic hard domain induced self-healable waterborne (polyurethane/acrylic) hybrid dispersions for 3D printable biomedical scaffolds

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Supporting Information Content

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Preparation of the monoglyceride of castor oil (MG_{CO})

MG_{CO} was prepared by glycerolysis of ester according to an earlier reported method.[1] Briefly, 4.6 g of castor oil (5 mM), 0.55 g of glycerol (6 mM), and 0.0023 g (0.055 wt% of castor oil) of calcium oxide (CaO) were taken in a three-neck round bottom flask equipped with a thermometer, a mechanical stirrer, and a nitrogen inlet. The reaction was performed at 225±2 ℃, and the solubility test (MG_{CO}: methanol = 1:3, at room temperature) confirmed the completion of the reaction.

Reactants/ Compositions	SWPUA-1	SWPUA-2	SWPUA-3	SWPUA-4
ϵ-PCL (mM)	1	1	1	1
DMPA (mM)	1.5	1.5	1.5	1.5
GECA (mM)	0.375	0.375	0.375	0.375
MG_{CO}(mM)	1	1	1	1
2-APDS (mM)	0.80	0.80	0.80	0.80
HMDA (mM)	0.35	0.35	0.35	0.35
IPDI (mM)	6.65	6.65	6.65	6.65
TEA (mM)	1.575	1.575	1.575	1.575
MMA (mM)	44.145	35.316	35.316	22.073
2-HEA (mM)	0	6.792	0	0
GMA (mM)	0	0	6.218	0
BA (mM)	0	0	0	17.241

Table S1. Recipes for the synthesis of SWPUAs with constant disulfide content (4.5 wt%).

Table S2. Various properties of monomers used in SWPUA preparation

Serial no	Properties	ε-PCL_{2000}	MMA	2-HEMA
1	Molecular weight (g mol^{-1})	2000	100.121	130.143
2	Melting point (℃)	60	-48	-12
3	Glass transition temperature (℃)	-60	-	-
4	Boiling point (℃)	-	101	250

Table S3. Particle size, zeta potential, and physical properties of SWPUAs and their films.

Sample	Appearance	Z-average size (nm)	Zeta potential (mV)	Molecular weight		PDI	Contact angle
				M_w (g/mol)	M_n (g/mol)		
SWPUA-1	Milky white	105.1	-50.6	173265	106876	1.621	84.7°
SWPUA-2	Milky white	135	-47.1	146783	91281	1.607	94.4°
SWPUA-3	Milky white	109.6	-50.0	151605	91996	1.647	86.1°
SWPUA-4	Milky white	115	-60.4	150189	92194	1.629	86.5°

Property	SWPUA-1	SWPUA-2	SWPUA-3	SWPUA-4
Tensile strength (MPa)	7.28±0.5	9.56±0.3	8.53±0.7	4.58±0.5
Strain (%)	524±2	145±2	217±4	484±3
Toughness (MJm^{-3})	34.43±0.8	12.65±0.5	15.12±0.5	19.52±0.7
Scratch hardness (kg)	2±0.02	2±0.02	2±0.01	2±0.02
T_1 (℃)	251.64	249.71	235.27	250.30
T_{MAX} (℃)	327.71	326.96	329.39	328.45
T_2 (℃)	418.21	422.08	415.53	419.55
T_g (℃)	54.38	46.89	47.14	39.38

Table S4. Mechanical and thermal properties of SWPUAs.

Table S5. Time required (s) for healing of SWPUA films under microwave radiation.

Power (W)	SWPUA-1	SWPUA-2	SWPUA-3	SWPUA-4
800	300	330	300	300
700	390	400	380	390
600	520	550	520	530

Table S6. Mechanical strength data of the SWPUA films after healing.

Samples	Healing Cycle	Tensile strength (MPa)	Healing efficiency (%)
SWPUA-1	1st	4.93±0.7	67.71
SWPUA-2	1st	5.30±0.2	55.44
SWPUA-3	1st	6.42±0.4	75.26
SWPUA-4	1st	3.78±0.2	82.53

Table S7. Mechanical data of the SWPUA films after reprocessing

Samples	Tensile strength (MPa)	Recycle efficiency (%)	Elongation at break (%)	Recycle efficiency (%)
R1 SWPUA-1	6.02±0.3	82.69	360±5	68.70
R1 SWPUA-2	8.85±0.2	92.57	126±2	86.89
R1 SWPUA-3	7.83±0.2	91.79	189±2	87.09
R1 SWPUA-4	3.55±0.4	77.51	417±2	86.15

Parameter/ composition	Cuboid	Disc
Dimension	2.5 cm × 2.5 cm × 2 cm (Length × width × height)	1.5 cm (ID), 2.9 cm (OD), 0.5 cm (Thickness)
Solution A	GelMA 20% (w/v)/ SWPUA-2, (1:1, v/v)	GelMA 20% (w/v)/ SWPUA-2, (1:1, v/v)
Solution B	Gelatin 20% (w/v)	Gelatin 20% (w/v)
Ink composition	Solution A/ Solution B (0.6:0.4, v/v)	Solution A/ Solution B (0.6:0.4, v/v), added a few drops of bromophenol blue indicator
Layer height	0.35 mm	0.25
Shell Thickness	0.40 mm	0.30
Fill density	20%	15%
Flow rate	20%	20%
Printing speed	6.0 mm/s	8.0 mm/s

Table 8. Optimized ink composition and machine parameters of the 3D printing.

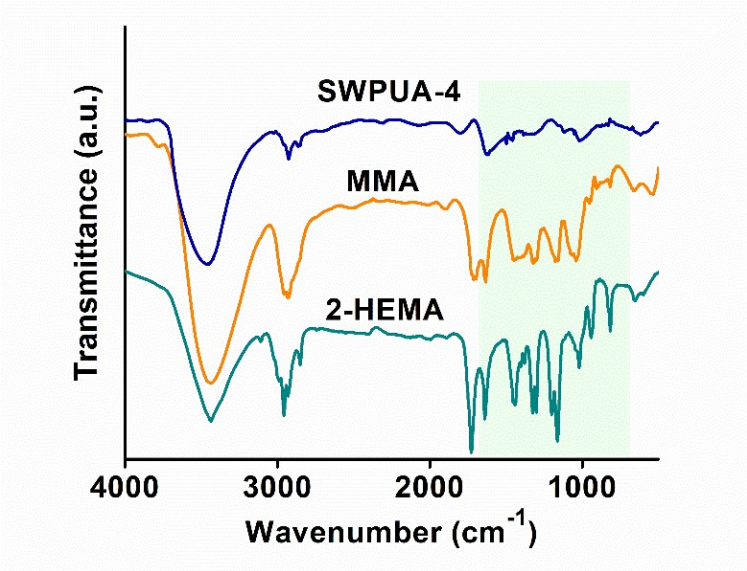

Fig S1. FTIR spectra of SWPUA-4, MMA monomer, and 2-HEMA monomer.

Again, verification of the presence of acrylate functionality (moiety) in SWPUA is indirectly proof from FTIR analysis. In an acrylate monomer, there is only C=C bond and –(C=O)-R (ester) groups are present as the primary functional groups. However, there would be no C=C bond after the free radical polymerization, which converted into C–C bond. Additionally, ester groups are not only present in acrylate moieties but also present in other moieties e.g., GECA, so it is very difficult to assigned them for a particular moiety after the polymerization. An FTIR spectra of MMA monomer, 2-HEMA, and SWPUA-4 was added in the ESI for demonstrating the change occurred in various vibrational frequencies before and after the polymerization. Specifically, absence of two peaks near 1638 cm^{-1} and 817 cm^{-1} corresponding to C=C bond stretching confirms the formation of interpenetrating polymer network (IPN) formation with polyurethane matrix.[2]

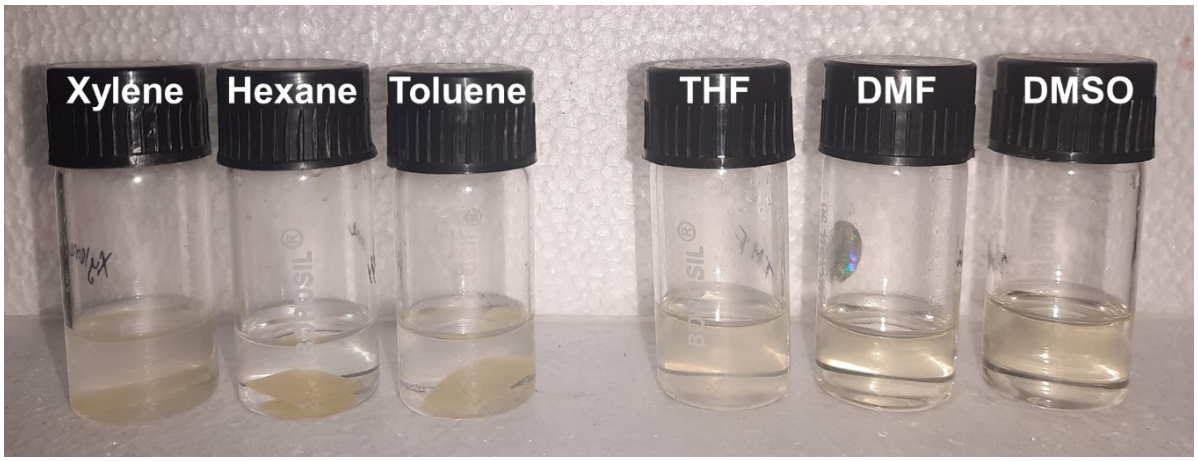

Fig S2. Solubility test of SWPUA-2 in various solvents.

It is pertinent to note that SWPUA consists of polyurethane and polyacrylic chains which are virtually or physically cross-linked not via the chemical covalent bond formation. Again, as SWPUA consists of enormous polar group such as ester, carbamate, urea, etc., so there are several polar-polar interactions present between the SWPUA system and polar solvent. These interactions lead to ionic/polar disintegration of polymeric chain and make the SWPUA soluble in the solvent.

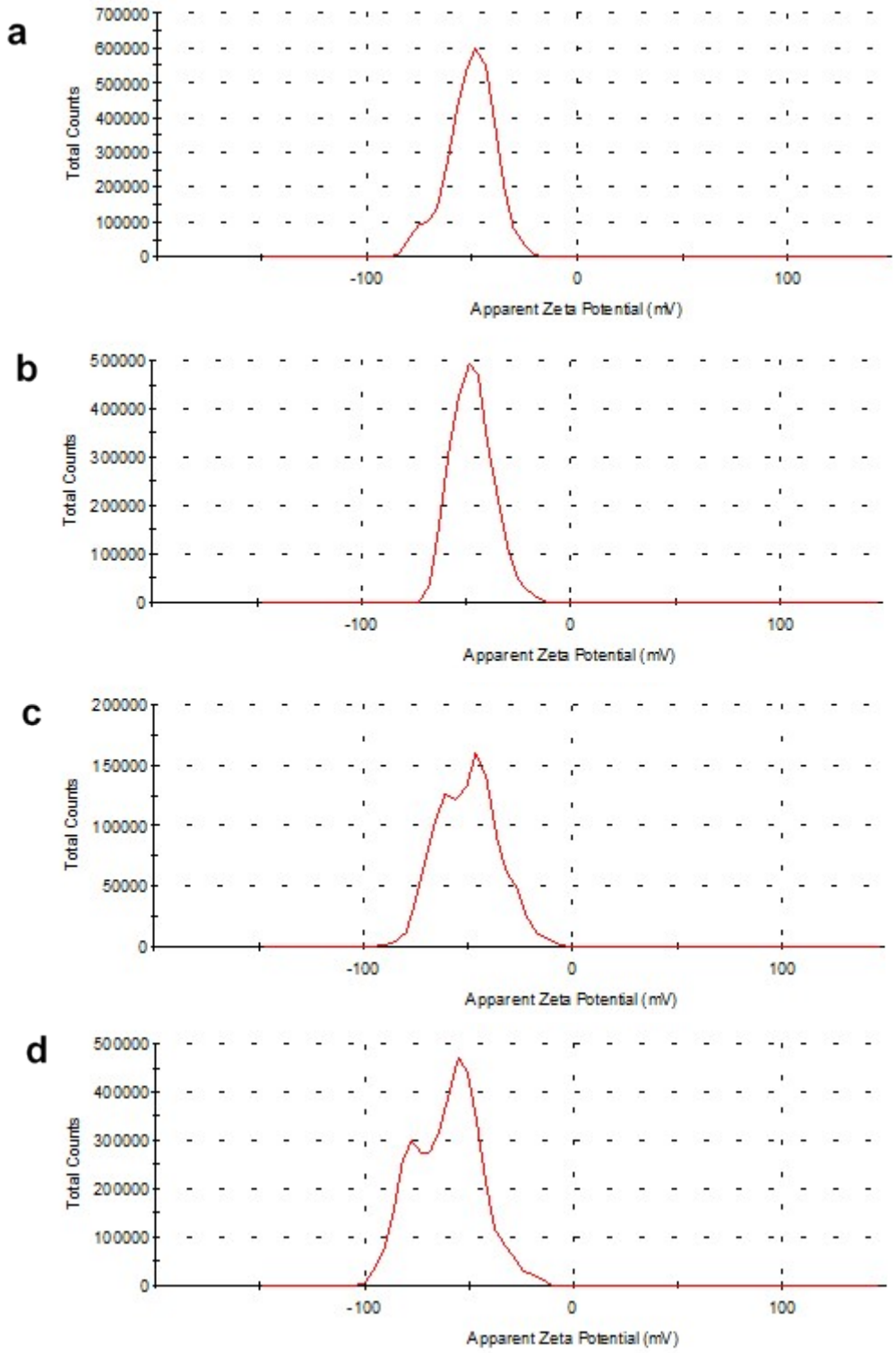

Fig S3. Zeta potential distribution curves for (a) SWPUA-1, (b) SWPUA-2, (c) SWPUA-3, and (d) SWPUA-4.

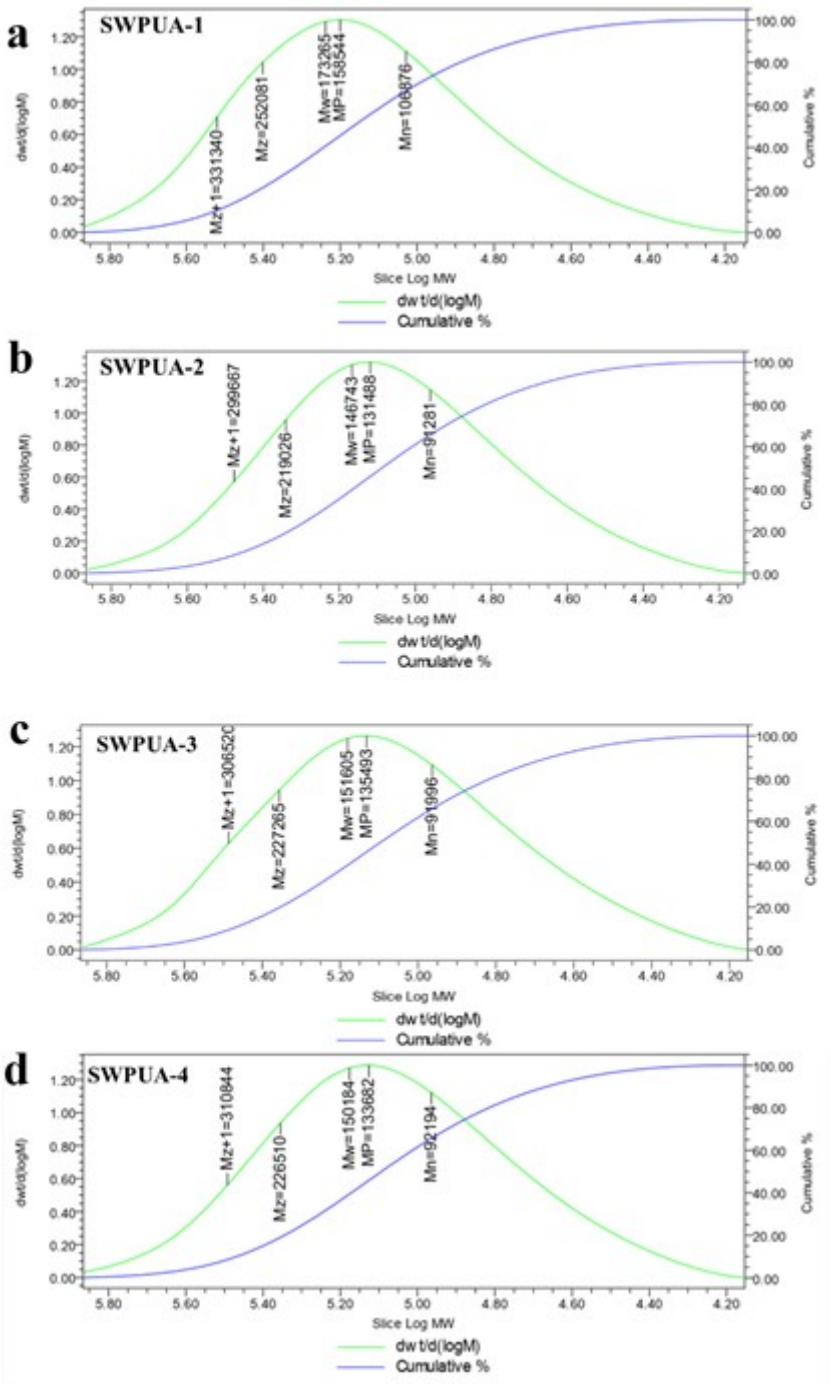

Fig S4. GPC chromatograms show average molecular weights of SWPUAs.

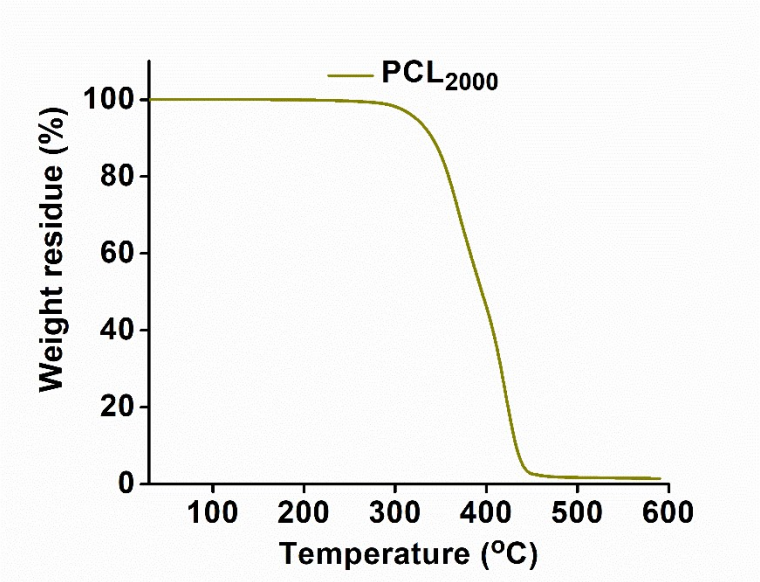

Fig S5. TGA curve of ε-PCL_{2000}

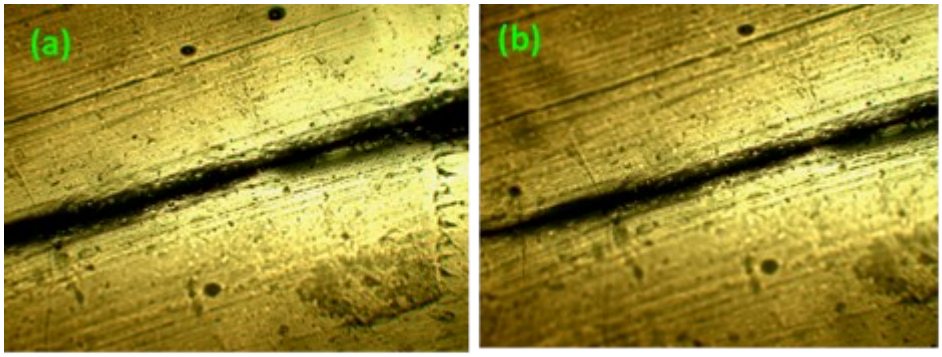

Fig S6. Optical microscopic images of PUA film (a) before and (c) after, healing test.

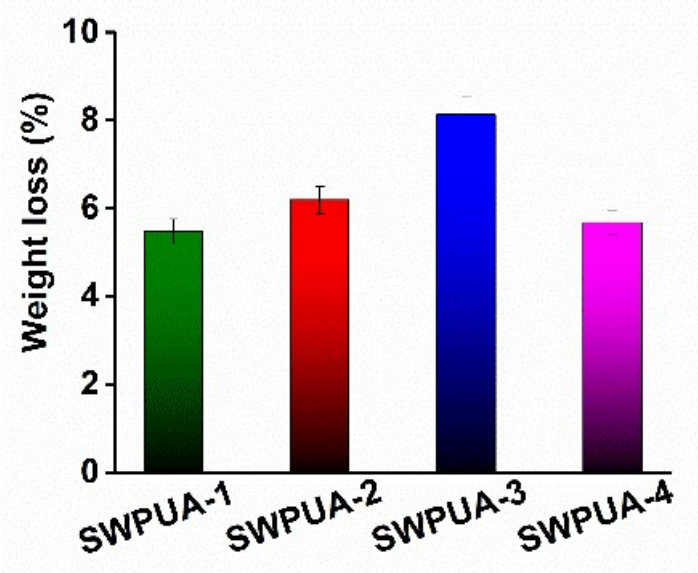

Fig S7. Weight loss (%) after 120 days of the soil burial test.

Movies

1. Movie S1. This movie shows the toughness of SWPUA-2 which can successfully lift a load of 4 kg.
2. **Movie S2.** This movie shows the stretchability after the healing of SWPUA-2.
3. Movie S3. This movie shows the 3D printability nature of SWPUA-2/GelMA/Gelatin.

References

1. H. Kalita and N. Karak, *J. Appl. Polym. Sci.*, 2014, **131**, 1−8.

2. D. Hamulić, P. Rodič, M. Poberžnik, M. Jereb, J. Kovač and I. Milošev, *Coatings,* 2020, **10**, 172.