

Dedicated to

Nan

Papa

My Famíly

My Neighbours

All Teachers

Æ

God

DECLARATION

I, do hereby declare that the thesis entitled "Smart Waterborne Polyurethane

Nanocomposites for Multifaceted Advanced Applications", submitted to the

Department of Chemical Sciences, Tezpur University, under the School of Sciences is

a record of original research work carried out by me. All sources of support and

assistance have been assigned with due acknowledgment. I, also declare that neither

this work as a whole nor any part of it has been submitted to any other University or

Institute for any kind of degree, diploma or award.

Place: Tezpur University, Tezpur

Date: 05/10/2023

Samikan Mokang

(Samiran Morang)

ii

TEZPUR UNIVERSITY



(A Central University Established by an Act of Parliament)
Napaam, Tezpur-784028, Sonitpur, Assam, India

Dr. Niranjan Karak Professor Department of Chemical Sciences Phone: +91-3712-267004 (O) Fax: +91-3712-267005 (O)

Email: nkarak@tezu.ernet.in

CERTIFICATE

This is to certify that the thesis entitled "Smart Waterborne Polyurethane Nanocomposites for Multifaceted Advanced Applications" submitted to Tezpur University, in the Department of Chemical Sciences, under the School of Sciences, in partial fulfillment for the award of the degree of Doctor of Philosophy in Science is a record of research work carried out by Mr. Samiran Morang under my supervision and guidance.

All help and assistance received by his from various sources have been duly acknowledged. No part of this thesis has been reproduced elsewhere for award of any other degree.

Place: Tezpur University, Tezpur

Date: 05 (10) 2023

(Dr. Niranjan Karak)

Professor

Department of Chemical Sciences

School of Sciences

Tezpur University

PREFACE

In the pursuit of addressing the continuously growing needs in the field of polymer science

and technology, extensive research is conducted on waterborne polyurethanes (WPUs) and

their nanocomposites (WPUNCs) to assess their adaptability and usefulness across a wide

range of applications. Among these endeavors, the creation of smart WPUs and WPUNCs by

judicial molecular engineering and incorporating carbon-based nanomaterials demonstrate

significant promise for high-performance applications, thanks to their exceptional and

distinctive properties. Again, contemporary circumstances have underscored the

importance of "going green" and embracing "sustainability" in scientific research, in

response to the global ecological challenges linked to the polymer industry. Hence, current

endeavors are dedicated to the development of environmentally friendly, economically

feasible, and industrially robust WPUs and WPUNCs by utilizing renewable resources such

as vegetable oil, glycerol, etc. These materials are suitable for a wide range of advanced

applications with smart features like shape memory, self-healing, photoluminescence, and

so forth.

Hence, this work introduces a novel perspective on the development of

environmentally friendly, high-performance WPUs and WPUNCs derived from renewable $\,$

resources, exhibiting unique properties and holding significant potential for various

contemporary applications.

Date: 05/10/2023

Place: Tezpur University, Tezpur

Samiran Morang

Samiran Morang

V

ACKNOWLEDGEMENTS

Guru Brahma Guru Vishnu Gurudevo Maheshwarah I Guru Sakshaat Parabrahma, Tasmae Shri Guruve Namahaa II

The journey from a state of innocence, through dreams of youthful adventure, to obtaining a Ph.D. would not have been fulfilling without acknowledging all those individuals who have actively contributed to its realization.

Above all, I extend my heartfelt gratitude to my Ph.D. supervisor, Prof. Niranjan Karak of the Department of Chemical Sciences at Tezpur University, for dedicating his full efforts to guide me in achieving my academic goals. From providing hands-on experimental training to encouraging critical thinking and the expression of ideas, his mentorship has left an indelible mark on my academic journey that I will carry with me throughout my life. His counsel to embody the determination of Arjuna from the Mahabharata echoed within me countless times, undoubtedly serving as a wellspring of motivation that propelled me forward and encouraged me to tackle fresh challenges throughout my Ph.D. expedition. Thank you Sir for everything.

I would like to extend my sincere gratitude and respect to my doctoral committee members, Prof. Ashim J. Thakur and Prof. Kusum K. Bania, Department of Chemical Sciences, Tezpur University, for their expertise and constructive feedback, which greatly enriched the quality of this work.

I extend my deepest gratitude to both the present and former Heads of the Department, Prof. Panchanan Puzari and Prof. Ruli Borah, respectively. Their unwavering support and provision of opportunities, ranging from

access to advanced instrumental facilities to fundamental departmental amenities, have played a pivotal role in facilitating the smooth progress of my research work.

I am profoundly grateful to my collaborators, namely Prof. Biman B. Mandal and Ashutosh Bandyopadhyay from the Department of Bioscience and Bioengineering at IIT Guwahati, Prof. Ramesh C. Deka and Nishant Biswakarma from Tezpur University, and Dr. Atharva Poundarik and Jay H. Rajput from IIT-Ropar, Punjab. Additionally, my thanks extend to Dr. Bodhisatwa Das and Anwesha Mukherjee, also from IIT-Ropar, Punjab. Their generosity in allowing me to conduct various biological experiments in their laboratories has been invaluable to my research.

I would like to extend my heartfelt gratitude to all the esteemed faculty members of the Department of Chemical Sciences for their invaluable suggestions and guidance. My sincere appreciation goes out to the dedicated official and support staff of the department for their indispensable efforts and assistance. Additionally, I would like to express my thanks to all the fellow scholars within the department for their friendly and supportive interactions.

I am wholeheartedly appreciative of the technical staff within the Department of Chemical Sciences, as well as those from SAIC (specially, Prakash da and Tridip da) and the Department of Physics at Tezpur University. Furthermore, my gratitude extends to CIF and NECBH, IIT-Guwahati for their invaluable support in offering instrumental and analytical assistance for my research.

I am deeply grateful to CSIR-HRDG, India, for their financial support, which has been instrumental in the progression of my research.

I extend my heartfelt appreciation to all the members of the APNL (Advanced Polymer and Nanomaterial Laboratory) family, including Dr. Geeti Kaberi Dutta, Dr. Tuhin Ghosh, Dr. Rajarshi Bayan, Dr. Rituparna Duarah, Dr. Deepshikha Hazarika, Dr. Aditi Saikia, and Dr. Dimpee Sarmah. Their valuable suggestions and guidance, delivered with genuine affection, have been of immense help in my academic journey.

I cannot express enough gratitude to my dearest colleagues and closest friends, Nobomi and Annesha, for their unwavering companionship, moral support, and for generously sharing their knowledge, which greatly enriched my academic journey. I am deeply appreciative of Kriti Yadav (affectionately known as "little one"), Raghav Poudel (for videography assistance), Kalyan Dutta, and Ashok Bora for their dynamic cooperation, affection, and care throughout my Ph.D. journey. The close-knit family I have found here has showered me with blessings and countless memories that I will cherish forever.

I would like to extend my heartfelt thanks to my dear friends, including Raju Chouhan, Pinku Saikia, Gautam Gogoi, Suranjana Patowary, Rashmi Chetry, Bikash Ch. Mushahary, Dolly Saikia, Bedanta Thakur, Mahari Basumatary, Raktim Gogoi, Surya K. Borah, Mahesh Dubey, and Debajit Bora. Additionally, my gratitude goes to my respected seniors Raktim Abha Saikia, Nishant Biswakarma, Rakhi Saikia, Chiranjita Goswami, and Sudhamoyee Kataky, for their invaluable assistance and support. I also want to express my thanks to all my well-wishers for their encouragements and supports.

I would like to extend my acknowledgment to Mrs. Susmita Karak for her love and care, which contributed to making my time here more enjoyable and memorable.

I want to convey my sincere gratitude to the Badminton Club at Tezpur University and my fellow game partners, such as Rahul, Manithoi, and

Subham, for helping me stay physically active and fit.

I am delighted to seize this moment to express my heartfelt appreciation to my family members: Nan, Papa, Sumi, Mon, Dhunda, Horunan, Aita, and Pehi, for their unwavering love and care. I attribute everything I have achieved today to the dedication and thirst for knowledge that my parents instilled in me. Their sacrifices, hard work, and unwavering support have brought me to this stage in my life. I am forever grateful to all my cousins and relatives for their affection and inspiration, which continually motivates me to surpass my limits and reach new heights.

Finally, I offer my heartfelt gratitude to Lord Krishna for His blessings and guidance, which have illuminated my path throughout my journey. I just want to say "god gives me everything".

Place: Tezpur University, Tezpur

Date: 05/10/2023

Samiran Morang)

LIST OF ABBREVIATIONS AND SYMBOLS

% Percentage

° Degree

°C Degree centigrade

 δ Chemical shift

 $\lambda \hspace{1cm} \text{Wavelength}$

ζ Zeta potential

 μL Microliter

μm Micrometer

0-D Zero dimensional

1-D One-dimensional

2-D Two-dimensional

a.u. Arbitrary units

A Ampere

AFM Atomic force microscopy

ASTM American society for testing and methods

ATR Attenuated total reflectance

cm Cenitmeter

CNFs Cellulose nanofibers

DLS Dynamic light scattering

DMAc N,N-dimethylacetamide

DMA Dynamic mechanical analysis

DMSO Dimethyl sulfoxide

DSC Differential scanning calorimetry

Eq Equation

eqv Equivalent

eV Electron volt

EDA Ethylene diamine

EDX Energy dispersive X-ray

FESEM Field emission scanning electron microscope

FTIR Fourier transform infrared

g Gram

g- C_3N_4 Graphitic carbon nitride

GECA Glycerol ester of citric acid

g/mol Gram per mole

GO Graphene oxide

GPa Giga pascal

GPC Gel permeation chromatography

h Hour

HDF Human dermal fibroblasts

HMDA 1,6-Heamethylene diamine

IPDA Isophorone diamine

IPDI Isophorone diisocyanate

J Joule

kg Kilogram

kN Kilo Newton

mg Milligram

 MG_{CO} Monoglyceride of castor oil

min Minute

mm Millimeter

mV Millivolt

MHz Mega hertz

M_n Number average molecular weight

M_w Weight average molecular weight

MPa Mega pascal

nm Nanometer

N Newton

NMR Nuclear magnetic resonance

OD Optical density

PCL Polycaprolactone

ppm Parts per million

RBC Red blood cell

rpm Rounds per minute

RGO Reduced graphene oxide

s Second

SEM Scanning electron microscope

SPR Surface plasmon resonance

TCP Tissue culture plate

TDA Toluene diisocyanate

TEM Transmission electron microscope

 $T_g \hspace{1cm} \hbox{Glass transition temperature} \\$

TGA Thermogravimetric analyser

 T_{MAX} Maximum degradation temperature

 T_{ON} Onset degradation temperature

 $T_p \hspace{1cm} Peak \, degradation \, temperature$

THF Tetrahydrofuran

UTM Universal testing machine

V Volume

UV Ultraviolet

VOC Volatile organic compounds

wt% Weight percent

XPS X-Ray photoelectron spectroscopy

XRD X-ray diffraction

SCHEME INDEX

Scheme No.	Scheme legend	Page No.
1.1	Common route for synthesis of polyurethane	1-8
1.2	Steps involves in pre-polymerization technique for WPU synthesis	1-19
2.1	Synthetic routes of GECA	2-9
2.2	General reaction pathway to synthesize PUD	2-11
3.1	The representative synthetic route for the synthesis of SWPUA dispersions	3-8
4.1	(a) Synthetic routes to WPU elastomers and cross-linked structure of GECA and (b) possible strong H-bonds developed between various groups (two urea groups, carbamate-urea groups, and two carbamate groups)	4-8
5.1	(a) Steps involved for preparing SHWPU and possible reversible interactions (covalent and non-covalent) and (b) disulfide metathesis in SHWPU.	5-6
6.1	Preparation of Mo@S-CN nanohybrid	6-6
6.2	Preparation of SHWPU/NS nanocomposite dispersions	

FIGURE INDEX

Figure No.	Figure legend	Page No.
1.1	Simple representations of (a) 0-D, (b) 1-D, and (c) 2-D nanomaterials	1-15
1.2	Structure of carbon-based nanomaterials	1-17
1.3	Preparative methods of nanomaterials	1-21
1.4	Applications of WPUs and WPUNCs	1-39
2.1	FTIR spectra of GECA and citric acid	2-9
2.2	(a) $^1\mathrm{H}$ NMR and c) $^{13}\mathrm{C}$ NMR spectra of GECA	2-10
2.3	(a) FTIR spectrum of the prepolymer, and (b) FTIR spectra of PUDs	2-12
2.4	(a) $^1\mathrm{H}$ NMR spectrum and (b) $^{13}\mathrm{C}$ NMR spectrum of PUD-2 film (representative one)	2-13
2.5	Optimized structures of DMPA (A), IPDI (B), and GECA (C)	2-14
2.6	Optimized structures of intermediates (IM), transition states (TS), and potential energy diagram for (a) A–B and (b) B–C species interaction at M06-2X/6-31+G (d, p)	2-16
2.7	(a-c) Average molecular weight, (d)water contact angle, (e) P-XRD spectra, and (f) percentage of transmittance of PUD films	2-18
2.8	Stress-strain profiles of PUD films	2-20
2.9	(a) TGA thermograms, (b) DTG curves, and (c) DSC curves, of PUDs	2-21
2.10	Stress-strain profiles of (a) PUD-1, (b) PUD-2, and (c) PUD-3, films after UV-aging for 135 h at 256 nm	2-23

2.11	(a) Change in optical density (OD) of bacterial solutions at 600 with time and (b-c) SEM images of control (un-degraded) and degraded films and their respective 3D-surface plot obtained from ImageJ software	2-24
3.1	(a) FTIR spectrum of the prepolymer of SWPUA-2 and (b) FTIR spectra SWPUAs	3-9
3.2	(a) $^1\mathrm{H}$ NMR spectrum and (b) $^{13}\mathrm{C}$ NMR spectrum of SWPUA-2	3-10
3.3	(a) Digital photos of SWPUA dispersions, (b) particle size distribution, (c) zeta potential (mV) of SWPUA dispersions, (d) TEM image of SWPUA-2 dispersion, (e) contact angle, and (f) percentage of transmittance of SWPUA films	3-12
3.4	(a) TGA thermograms, (b) DTG curves, (c) DSC curves of SWPUA films	3-14
3.5	(a) Stress-strain profiles, (b) toughness of SWPUAs, and (c) showing a load of 4 kg lifted using an SWPUA-2 film	3-15
3.6	(a) Possible healing mechanism, (b) three pieces of the cut film before healing and joined the film after healing at 800 W for 330 s, (c-f) stress-strain profile of SWPUA film after 1st cycle of healing at 800 W for 330 s, (g-h) optical microscopic images of crack and healing films (SWPUA-2), and (i-j) stretching and weight-lifting test after healing of SWPUA-2	3-18
3.7	(a-b) Digital images of reprocessed SWPUA-2 film at 60 °C with a pressure of 60-80 kg cm-2 in 30 min, (c) stress-strain profiles of SWPUA-2 after 1st cycle (R1 SWPUA-2) of reprocessing, (d) tensile strength recovery (%) of SWPUA film after 1st cycle of reprocessing, and (e) TGA thermograms of pristine and reprocessed SWPUA-2 film	3-19
3.8	Cell viability studies of L929 cells treated with different concentrations of SWPUA-2 solution (10%, 20%, 30%) after 24 h and 72 h	3-20
3.9	(a-d) Bright-field micrographs, (e-h) Live/dead staining of L929 cells treated with control and various percentages of SWPUA-2 solution (10%, 20%, and 30%) after 3 days of incubation	3-20
3.10	(a) 3D slicing model of cuboid and disc and (b-c) 3D bioprinted cuboid and disc scaffolds before and after drying	3-22
3.11	Tafel Plots for coated and uncoated samples at (a) 0 th and (b) (a) Weight loss (%) after 120 days of the soil burial test, (b-c) SEM images of controlled (un-degraded) and degraded films of SWPUA-2, respectively, and (d-e) 3D surface plots of the SEM images obtained from ImageJ software	3-23

4.1	FTIR spectra of NCO-terminated prepolymer and WPUs	4-9
4.2	(a) $^1\mathrm{H}$ NMR and (b) $^{13}\mathrm{C}$ NMR spectra of WPU-HI-2	4-10
4.3	(a) Digital images of WPUs (at actual scale, 2.5 mL Eppendorf), (b) particle size distribution, (c-d) TEM images of WPU-HI-2 (0.2 μm, and 50 nm, (e) P-XRD spectra of WPUs, (f) percentage of transmittance of WPU films of thickness 0.10 mm, in set: The word " transparent " can be easily visible through the WPU-HI-2 film (thickness 0.10 mm), and (g-k) water contact angle of WPUs	4-11
4.4	(a) TGA thermograms, (b) first order derivative curves (dTG),	4-13
	(c) DSC curves of WPUS	
4.5	(a) Stress-strain profiles, (b) maximum stresses (MPa), (c) percentages of maximum strain at break of WPU films, (d) Digital images of stretchability (> 6000%) of WPU-H, (e) 3D-variations of toughness (MJm-3), mechanical strength (MPa), and strain (%) of all WPU films, and (f) photograph demonstrate that WPU-HI-3 film (0.66g) can lift more than 10 kg weight	4-14
4.6	(a) Stress-strain profile of un-notched and notched WPU-I film, (b) fracture energy of all WPUs, (c) the process of fracture test for WPU-I, and (d) the puncture test on WPU-HI-3 (thickness of 0.8 mm) using a screw-driver with a tip of diameter 1.35 mm	4-15
4.7	(a) No loss of structural integrity after spreading $0.2~\mu L$ of DMF on the surface of WPU-I, (b) stress-strain profiles of WPU-I before and after healing at $90~^{\circ}C$ for $2~h$, (c) percentage of healing efficiency of WPUs, (d) stress-relaxation curves of WPU films at two different temperatures (RT and $90~^{\circ}C$) and in presence of DMF, provided fixed strain of 10% for $15~min$, (e-f) ATR spectra of the WPU-I specimen after being contacted with trace DMF, (g) weight lifting after healing (WPU-HI-2, 4 kg), (h) stretching test after healing, and (i-j) optical microscopic images of cut film and healed film of WPU-I	4-16
4.8	Shape memory test of WPU-HI-3 (a-e) under warm water at 70 °C and (f-i) WPU-HI-2 under microwave radiation (900W)	4-19
4.9	(a) Small pieces of used films and a reprocessed film, (b) TGA thermograms, and (c) stress-strain profiles of pristine WPU-I and reprocessed WPU-I (R¹-WPU) films (recovery efficiency-stress of 86.94% & strain of 85.77%)	4-20
4.10	(a) Representative rhodamine-phalloidin stained micrographs of platelets adherance on (i) collagen coated surface, (ii) WPU-H, (iii) WPU-HI-1, (iv) WPU-HI-2, (v) WPU-HI-3, and (vi) WPU-	4-21

	I, b) LDH activity of the platelets adhered on the various WPU surfaces as compared with collagen as positive control, (c) RBC lysis caused by PC (20% Triton-X 100), Saline (150mM NaCl) and various WPU surfaces measured optically, and (d) degradation of various films on days 15, 30, 45 and 60 days incubated in 0.1M PBS expressed as weight percentage degraded. (n=3, *p≤0.05 and **p≤0.001, scale bar: 200 μm)	
4.11	(a) Alamar blue based cellular proliferation of HDF seeded on various WPU surfaces and TCP (Tissue Culture Plate), (b) reduced alamar units on day 7 depicting the variation in proliferation of HDF on various surfaces. (n=4, *p≤0.05), (c) representative micrographs showing live-dead imaging after 7 days of incubation in Control (Tissue Culture Dish) and WPUs, and (d) representative micrographs showing phalloidin-DAPI imaging after 7 days of incubation in Control (Tissue Culture Dish) and WPUs showing the cytoskeleton and the nuclei (scale bar: 200 µm)	4-22
4.12	(a) Change in the optical density (OD) of the <i>B. subtilis</i> bacterial solution with WPU films, (b) weight residue after 2 months of microbial exposure; SEM images of (c-1) controlled (before biodegradation) and (d-1) biodegraded of WPU-HI-2 film, and (c-2 and (d-2) surface 3D plots of SEM images obtained from ImageJ software	4-24
5.1	FTIR spectra of SHWPU-1 prepolymer and SHWPUs	5-7
5.2	(a) $^1\mathrm{H}$ and (b) $^{13}\mathrm{NMR}$ spectra of SHWPU-2	5-8
5.3	(a) Digital images of SHWPUs dispersion keeping in Eppendorf tube, (b) particle size distribution curves, (c) TEM images of SHWPU-2 dispersion (100nm), (d) powder X-ray diffraction (P-XRD) patterns, (e) percentage of transmittance spectra, inset: a small heart is visible through the SHWPU-4 film, and (f) contact angle of SHWPUs film	5-9
5.4	(a) TGA thermograms, (b) DTG curves, and (c-d) DSC curves of SHWPU films	5-12
5.5	(a) Stress-strain profiles, (b) 3D curve of toughness of SHWPU films, (c) stress-strain profile of the SHWPU-3 elastomer divided into three regimes, (d) digital photos showing the whitening process of SHWPU-3 with increase in strain (%), and (MJm-3), maximum tensile stress (MPa), and strain (%) of all SHWPU films, (e) lifting a dumbbell of 25 kg using SHWPU-3 (0.466 g), (f) stress-strain curve of un-notched and notched (1 mm) SHWPU-4 film, (g) fracture energy of SHWPUs determined using Greensmith's method, (h-j) digital photos of fracture test (SHWPU-2), and (k) puncture test of SHWPU-4	5-14

5.6	(a) Graphical illustration of the healing process, stress-strain profiles of (b) pristine and healed SHWPU-1 film at 140 ± 5 °C for 2h without DMF, (c) pristine and healed SHWPU-4 films heated at 110 ± 5 °C for different times (2h, 0.5h, and 10 min) with DMF, (d) healing efficiency (%) of SHWPUs, (e) weight lifting test (8 kg), (f) stretching test for SHWPU-3 after healing, and (g-h) optical microscopic images before and after healing (scale = $100~\mu m$)	5-16
5.7	(a) Plausible mechanism of the shape recovery process, (b) shape recovery test underwater at 80 °C, (c) reprocessing of SHWPU-4 films at 80 °C under a pressure of 60-80 kg cm ⁻² , (d) FTIR spectra, (e) TGA thermograms, and (f) stress-strain profile, of the pristine and reprocessed SHWPU-4 film	5-18
5.8	(a) Representative rhodamine-phalloidin stained micrographs of platelets adhere on (i) collagen coated surface, (ii) SHWPU-1, (iii) SHWPU-2, (iv) SHWPU-3, and (v) SHWPU-4, (b) LDH activity of the platelets adhered on the various SHWPU surfaces as compared with collagen as the positive control, (c) RBC lysis caused by PC (positive control) (20% Triton-X 100), saline (150mM NaCl) and various SHWPU surfaces measured optically, and (d) degradation of various films on days 15, 30, 45 and 60 days incubated in 0.1M PBS expressed as weight percentage degraded. (n=3, **p≤0.001) (scale bar: 200 μm)	5-20
5.9	(a) Alamar blue-based cellular proliferation of HDF seeded on various SHWPU surfaces and control (TCP), (b) reduced Alamar units on day 7 depicting the variation in a proliferation of HDF on various surfaces. (n=4, **p≤0.01), (c) representative micrographs showing live-dead imaging after 7 days of incubation in control, SHWPU-1, SHWPU-2, SHWPU-3, and SHWPU-4 (Scale bar: 200 μm)	5-22
5.10	(a-b) 'Artificial muscle' contraction stimulate by temperature (80 °C), (c-f) digital images of various steps during lifting a weight of 100 gm at 80 °C for 120 s, scaffold before drying, (g) gelatin (20 % w/v) /SHWPU-2 (1:0.5), (h) gelatin (20 % w/v) /SHWPU-2 (1:0.3), (i, j & k) two, four, and six layers of gelatin (20 % w/v) /SHWPU-2 (1:0.3), (l) side view of six-layered gelatin (20 % w/v) /SHWPU-2 (1:0.3), and (m-r) scaffold after drying at 50 °C for 48 h	5-24
5.11	SEM images of (a-1) un-degraded and (b-1), degraded SHWPU-4 film and (a-2 and b-2) surface 3D plots of the corresponding SEM images obtained from ImageJ software	5-25
6.1	(a) SEM image, SEM (EDS) elemental mapping of (b) carbon, (c) nitrogen, (d) oxygen, (e) sulfur, and (f) molybdenum, (g) EDS spectrum, (h) FESEM image (scale: 1μm), TEM images at various scale (i) 200 nm; inset: SAED pattern, Size scale (j) 50 nm, and (k) 20 nm of Mo@S-CN nanohybrid	6-7

6.2	(a) Zeta Potential (mV), (b) P-XRD curves, (c) FTIR spectra, of bulk S-CN, bulk Mo@S-CN and Mo@S-CN nanohybrid, (d) UV-absorption spectra, (e) normalized PL spectra of bulk Mo@S-CN and Mo@S-CN nanohybrid, inset: the color change of exfoliated Mo@S-CN nanohybrid solution before and after UV-light (254 nm) illumination, (f) PL spectra of Mo@S-CN nanohybrid aqueous solution excited at a range of wavelength, (g) XPS survey spectrum of Mo@S-CN nanohybrid and high-resolution peak fitting spectra of (h) C 1s, (i) N 1s, (j) O 1s, (k) S 2p, and (l) Mo 3d	6-8
6.3	(a) FTIR spectra, (b:1-4) digital images for nanocomposite dispersions, (c) Zeta potential (mV), (d) P-XRD spectra, of SHWPU/NS nanocomposites, (e) the percentage of transmittance (thickness ~0.15 mm), and (f) water contact angle, of SHWPU/NS films	6-10
6.4	(a) TGA thermograms and (b) DTG curves of SHWPU/NS nanocomposite films	6-13
6.5	(a) Stress-strain profiles, (b) toughness (MJm ⁻³), of SHWPU/NS nanocomposite films, (c) weightlifting test by using SHWPU/NS _{0.5} film, (d) stress-strain curves of un-notched and notched SHWPU/NS _{1.5} film, (e) fracture energies (MJm ⁻²), and (f) representative digital photos of fracture test on SHWPU/NS _{1.5} film	6-15
6.6	(a) Possible reversible dynamic interactions and healing mechanism, (b) stress-strain profiles of SHWPU/NS _{1.5} film before and after healed at 110 ± 5 °C for 1h and 2h using approximately 0.2 μ L of DMF, (c) SH efficiency (%) of SHWPU/NS nanocomposite films, (d) weightlifting test (8 kg), (e) stretching test, after healing, and (f-g) optical microscopic images of cut and healed film (SHWPU/NS _{1.5} film) (scale: 100 μ m)	6-16
6.7	(a) Representative phalloidin stained micrographs of platelets adhered to (i) collagen, (ii) Mo@S-CN nanohybrid suspension coated surfaces, and (iii) SHWPU/NS _{1.5} disc. (scale bar: 200 μ m), (b) LDH activity of platelets adhered to collagen, S SHWPU/NS _{1.5} disc and Mo@S-CN nanohybrid coated surfaces, (c) RBC lysis denoted by the absorbance in the presence of Triton-X100 (PC), saline, Mo@S-CN nanohybrid coated surfaces and SHWPU/NS _{1.5} discs, (d) Alamar based cellular proliferation on day 1, 3 and 7, and (e) alamar based proliferation index on day 7 for TCP, Mo@S-CN nanohybrid coated surfaces and SHWPU/NS _{1.5} discs. (n=3, #p \leq 0.001, *p \leq 0.05).	6-18
6.8	Representative live-dead stained micrographs of human dermal fibroblasts on day 7 when cultured on (a) Mo@S-CN nanohybrid coated surfaces, (b) SHWPU/NS-1.5 and (c) 2D	6-19

	control tissue culture dishes. (i) Merged image, (ii) represent the live (green channel) cells and (iii) represent the dead (red channel) cells. Representative phalloidin-DAPI stained micrographs of human dermal fibroblasts on day 7 when cultured on (d) Mo@S-CN nanohybrid coated surfaces, (e) SHWPU/NS-1.5, and (f) 2D control tissue culture dishes. (i) Show merged images, (ii) represent the nucleus (blue channel) of the cells, and (iii) represent the cytoskeleton (green channel) of the cells	
6.9	(a) and (b) Representative unstained micrographs of human dermal fibroblasts under various excitations; (i) 365 nm excitation, (ii) 470 nm excitation, (iii) 545 nm excitation, (iv) brightfield images, and (v) merged images	6-20
6.10	(a) Encryption application of the luminescent image in the virtual military scenario, the appearance of the word "APNL" written by using SHWPU/NS _{1.5} dispersions in the presence of (b) white light, (c) UV-365 nm, and (d) UV-254 nm light	

TABLE INDEX

Table No.	Table legend	Page No.
1.1	Commonly used diisocyanates in PU	1-9-10
1.2	Commonly used macroglycols in PU	1-11-12
1.3	Some common chain extenders used in PU synthesis	1-13
1.4	Common catalysts used in PU synthesis	1-14
2.1	Recipes for the synthesis of PUDs with a constant amount of $\varepsilon\text{-PCL}$ (2 mM, 4 g)	2-6
2.2	The DFT-based reactivity descriptors (in eV) of DMPA (A), IPDI (B) and GECA (C)	2-15
2.3	Physical properties of PUDs and their films	2-17
2.4	Mechanical properties and adhesive strength of PUDs	2-19
2.5	Thermal properties of PUD films	2-20
2.6	Weight loss (%) of PUDs in different chemical media	2-22
3.1	Recipes for the synthesis of SWPUAs with constant disulfide content (4.5 wt%)	3-4
3.2	Physical properties of SWPUAs and their films	3-11
3.3	Thermal properties of SWPUAs	3-13
3.4	Mechanical properties of SWPUA films	3-15
3.5	Time required for healing of SWPUA films under microwave radiation	3-16
3.6	Mechanical properties of the SWPUA films after healing at $800\mathrm{W}$	3-17
3.7	Mechanical data of the SWPUA films after reprocessing	3-19

3.8	Optimized ink composition and machine parameters of the 3D printing	3-21
4.1	Chemical compositions of the reactants for preparing WPUs	4-4
4.2	Shape memory property of WPU films	4-18
5.1	Chemical compositions of the reactants for preparing SHWPU dispersions	5-4
5.2	Characteristic parameters of SHWPUs obtained from TGA and DSC analyses	5-11
5.3	Mechanical properties of the SHWPU films	5-13
5.4	Mechanical data of the SHWPU films after self-healing at 110±5 $^{\circ}\mathrm{C}\text{for}$ 2h	5-15
5.5	The shape memory effect of SHWPU films	5-17
5.6	The optimized machine parameters and ink compositions	5-23
5.7	Weight loss percentage after 2 months of soil burial test	
6.1	The thermal parameters of SHWPU/NS nanocomposite films derived from TGA and DSC analyses	6-12
6.2	Mechanical properties of the SHWPU/NS nanocomposite films	6-14