

DROPLET BEHAVIOUR ON METASTABLE HYDROPHOBIC AND SUPERHYDROPHOBIC NONWOVEN MATERIALS

SUMIT SHARMA



**DEPARTMENT OF TEXTILE AND FIBRE ENGINEERING
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by

SUMIT SHARMA

Department of Textile and Fibre Engineering

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***Dedicated to my maternal grandmother
(Nani Ji)***

CERTIFICATE

This is to certify that the thesis entitled “**Droplet Behaviour on Metastable Hydrophobic and Superhydrophobic Nonwoven Materials**” being submitted by **Mr. Sumit Sharma**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Textile and Fibre Engineering, is a record of bonafide research work carried out by him. Mr. Sumit Sharma has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

Prof. Amit Rawal

Date:

Professor
Department of Textile and Fibre Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi -110016
India

Place:

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Abstract

Wetting is the most fundamental interaction between a solid and a liquid that modulates the spreading of the liquid through a balancing act of adhesive and cohesive forces. A hydrophobic surface is formed when the cohesive forces between the liquid molecules are stronger than the adhesive forces that exist between the liquid and solid molecules. Introducing nano- and/or micro-scale roughness on a hydrophobic surface or, alternatively, a micro/nanostructured rough surface coated with a hydrophobic layer tends to form a superhydrophobic surface. The macroscopic contact angle of a water droplet on the regular surfaces in the form of pillars and posts is well-understood and has been quantified in the literature. However, nonwoven materials consist of disordered and irregular arrays of fibres, bonded by friction and/or cohesion and/or adhesion. These materials have been sporadically investigated theoretically for the metastable and superhydrophobic states of the liquid droplet. Unfolding the intricate three-dimensional (3D) structure of nonwoven materials is a prerequisite to obtain the structural parameters that can serve as key inputs for predictive modelling. In this research work, a roadmap to gain insights into the metastable hydrophobic and superhydrophobic states of the liquid droplet on various nonwoven materials and their self-similar counterparts is presented by formulating a toolbox of analytical models. Key design parameters in the form of roughness factor and area fraction of fibres in contact with the liquid have been quantified.

With the aid of X-ray micro-computed tomography (micro-CT) analysis, the fibre and structural parameters, including fibre diameter, pore-size distribution, nonwoven porosity, and fibre orientation distribution, have been quantified. Some of these structural parameters served as key inputs for predicting the apparent contact angle in the metastable hydrophobic state of the liquid. The metastability of the wetting state is also confirmed via the highly diverse behaviour of water droplets ranging from rolling off or gradual absorption at various inclination angles to strong adhesion. Various combinatorial strategies to obtain hybrid wetting regimes have been designed and developed based upon self-similarity. A facile, scalable, and inexpensive vacuum filtration process has assisted in creating self-similar arrays of multi-walled carbon nanotubes (MWCNTs) and nonwoven fibres. A simple analytical model has been proposed to predict the apparent contact angle by

formulating a direct relationship with the structural parameters of MWCNTs and nonwoven materials. In general, a satisfactory agreement has been observed between the theoretical and experimental apparent contact angles of MWCNT decorated nonwoven materials.

On the other hand, spray-coating has been utilised to decorate the weakly hydrophobic stearate-treated titanate nanowires (TiONWs) on the surface of the nonwoven material. This has led to the self-similar nonwoven-titanate nanostructured materials (SS-Ti-NMs) that resulted in a superhydrophobic effect (contact angle $>150^\circ$ with roll-off angles in the vicinity of 10°). In SS-Ti-NMs, the 3D nonwoven material houses the air pockets in the bulk of the material along with the water repellent TiONWs on the surface resulting in superhydrophobic behaviour. Laser scanning confocal microscopy has confirmed the presence of a thin layer of water on the finer fibre SS-Ti-NMs. The governing design principles that underpin the key determinants responsible for the robust superhydrophobic behaviour have been unravelled. A comparison between theory and experiments has resulted in a good agreement. The present work also uncovers a wettability gradient across the thickness of SS-Ti-NMs in addition to the unusual display of underwater superhydrophobic behaviour. The current research work paves the way for several unexplored possibilities of nonwoven applications in the fields of energy storage, sensing, protective and biocidal garments, flexible and low-cost chemically active systems, and many more.

सार

गीला होने की प्रक्रिया किसी ठोस और द्रव्य पदार्थ के बीच होने वाली मूलभूत अंतःक्रिया है जो द्रव्य पदार्थ के फैलने की क्रिया को आसंजक और ससंजक बल के संतुलन द्वारा नियंत्रित करती है। जब द्रव्य अणुओं के मध्य ससंजक बल द्रव्य तथा ठोस पदार्थ के मध्य रहने वाले आसंजक बल से अधिक होता है तो ठोस पदार्थ की सतह जलविरोधी हो जाती है। किसी जलविरोधी सतह पर नैनो या माइक्रो माप के खुरदुरेपन की समाविष्टि करने, या फिर विकल्पिक रूप से, किसी नैनो या माइक्रो माप पर संरचित खुरदुरी सतह पर जलविरोधी परत लगाने से अतीजलविरोधी सतह बनती है। स्तंभों से आवृत सामान्य सतहों पर दृष्टिगोचर स्पर्श कोण को शोध साहित्य में भलीभांति समझा तथा परिमाणित किया गया है। तथापि नॉनवोवन पदार्थ अव्यवस्थित तथा अनियमित क्रम में लगे रेशों द्वारा गठित होते हैं, जोकि घर्षण, ससंजन या आसंजन द्वारा बद्ध होते हैं। इन पदार्थों की सतह पर द्रव्य बूंदों की मितस्थायी जलविरोधी तथा अतीजलविरोधी स्थिति का विकीर्ण विवेचन ही मिलता है। नॉनवोवन पदार्थ के त्रि-आयामी स्वरूप को प्रकट करना संरचनात्मक मापदंड प्राप्त करने के लिए पूर्वप्रेक्षित हैं। ये संरचनात्मक मापदंड पूर्वानुमान लगाने वाले मॉडल्स के लिए प्रमुख निविष्टि हैं। इस शोधकार्य में, नॉनवोवन पदार्थ तथा उनके स्व-सम प्रतिरूपों पर द्रव्य बूंद की मितस्थायी जलविरोधी और अतीजलविरोधी स्थिति को अंतरदृष्ट करने के लिए वैश्लेषिक मॉडल प्रतिपादित किए गए हैं। खुरदुरेपन को तथा नॉनवोवन के रेशों के द्रव्य पदार्थ के साथ संपर्क में आने वाले प्रभाग को निर्धारित करने वाले प्रमुख घटकों को भी इस शोधकार्य में परिमाणित किया गया है।

एक्स-रे माइक्रो-कंप्यूटेड टोमोग्राफी की सहायता से रेशों और नॉनवोवन के संरचनात्मक मापदंड जैसे की रेशों के व्यास, छिद्र के नाप का वितरण, नॉनवोवन की छिद्रिलता, ओर रेशों के दिग्विन्यास के वितरण को परिमाणित किया गया है। इनमें से कुछ मापदंडों का प्रयोग द्रव्य पदार्थ की मितस्थायी जलविरोधी स्थिति में आभास होने वाले स्पर्श कोण के पूर्वानुमान में किया गया है। नॉनवोवन पदार्थ पर बूंदों का व्यवहार, जो लुढ़कने, कुछ ढाल मिलने पर धीरे-धीरे अवशोषण होने से लेकर दृढ़ चिपकाव तक गोचर होता है से जलविरोधी होने की मितस्थायी स्थिति निश्चित होती है।

विविध प्रकार की सांयोगिक युक्तियों से स्व-सम प्रणाली पर आधारित गीले होने की मिश्रित स्थितियों का परिकलन किया गया है । एक सुगम, बड़े स्तर पर उपयोग किए जा सकने वाली, तथा मितव्ययी वैक्यूम फिल्टरन प्रक्रिया द्वारा बहु-प्राचीरीय कार्बन नैनोट्यूब्स (एम. डब्लू. सी. ऐन. टी) और नॉनवोवन रेशाओं के स्व-सम शृंखलाओं का निर्माण किया गया है । इन सतहों पर आभास होने वाले द्रव्य पदार्थ के स्पर्श कोण का एक सहज वैश्लेषिक मॉडल प्रस्तावित किया गया है जोकि एम. डब्लू. सी. ऐन. टी तथा नॉनवोवन पदार्थ के संरचनात्मक मापदंडों के मध्य एक सीधा संबंध प्रतिपादित करता है । सामान्यतः, पूर्वानुमानित और परीक्षण पर आधारित स्पर्श कोणों में एक संतोषप्रद सामंजस्य पाया गया है ।

दूसरी तरफ, स्प्रे-कोटिंग (छिड़काव द्वारा विलेपन) का प्रयोग कर मंद रूप से जलविरोधी टाईटेनेट नैनोवायर्स (टी. आई. ओ. ऐन. डब्लू.स.) को नॉनवोवन की सतह पर अलंकृत किया गया है । इस प्रकार स्व-सम नॉनवोवन-टाईटेनेट नैनोसंरचित पदार्थ (ऐस. ऐस.- टी. आई.- ऐन. ऐम्स.) बनाए गए हैं । ये पदार्थ अतीजलविरोधी प्रकृति (जल स्पर्श कोण $> 150^\circ$ और 10° से कम ढाल पर लुढ़कने का स्वभाव) दर्शाते हैं । त्रि-आयामी नॉनवोवन पदार्थ के अंदर रहने वाली वायु कोटरिकाओं तथा सतह पर जलविरोधी टी. आई. ओ. ऐन. डब्लू.स. के परिणामस्वरूप ये अतीजलविरोधी प्रकृति का सृजन होता है । लेसर क्रमवीक्षण कोनफोकल सूक्ष्मदर्शिका द्वारा सूक्ष्मतर रेशों से बने ऐस. ऐस.- टी. आई.- ऐन. ऐम्स. की सतह पर पानी की एक महीन परत की पुष्टि की गई है । सुदृढ़ अतीजलविरोधी व्यवहार का निर्धारण करने वाले अधिनियंत्रक परिकलन सिद्धांतों को विस्तार से बताया गया है । पूर्वानुमान और प्रयोगों में उत्तम सम्मति पाई गई है । इस कार्य में, जलमग्न अतीजलविरोधी व्यवहार के अतिरिक्त ऐस. ऐस.- टी. आई.- ऐन. ऐम्स. में गीलेपन का एक ग्रेडिएन्ट भी उद्घाटित किया गया है। वर्तमान शोधकार्य नॉनवोवन के ऊर्जा संचयन, संवेदन, रक्षात्मक, जैवनाशी, लचीले और अल्प-दरीय रसायन सक्रिय प्रणाली, सहित कई समुप्रयोगों के लिए मार्ग अनन्वेषित करता है ।

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Nomenclature

α	Slope of sinusoidal asperity
α_{max}	Maximum slope of asperity
β, γ	Out-of-plane fibre orientation angles
φ, ζ	In-plane fibre orientation angles
γ_{sl}	Interfacial tension/energy at solid-liquid interface
γ_{la}	Interfacial tension/energy at liquid-air interface
γ_{sa}	Interfacial tension/energy at solid-air interface
$\delta\theta$	Sagging angle
ϵ_c	Compressive strain
ϵ_g	Gravimetric porosity
ϵ_t	Transverse strain
ϵ_l	Longitudinal strain
ξ	Side of the square boxes used in Box-counting method
θ	Contact angle
θ_{eq}	Equilibrium contact angle
θ_a	Advancing contact angle
$\theta_{a,c}$	Critical advancing contact angle
θ_r	Receding contact angle
θ^*	Apparent contact angle
θ_W^*	Apparent contact angle of droplet in Wenzel's state
θ_{a-CB}^*	Advancing contact angles on porous surfaces exhibiting Cassie-Baxter state of wetting
θ_{r-CB}^*	Receding contact angles on porous surfaces exhibiting Cassie-Baxter state of wetting
θ_{CB}^*	Apparent static contact angle of a droplet in Cassie-Baxter's state of wetting
θ_{max}^*	Maximum apparent contact angle
θ_{min}^*	Minimum apparent contact angle
α_{max}	Maximum slope of asperity
θ_c	Critical contact angle
$\theta_{W,1}^*$	Apparent contact angle for coarse-scale roughness in Wenzel state of wetting

$\theta_{CB,1}^*$	Apparent contact angle for coarse-scale roughness in Cassie-Baxter state of wetting
$\theta_{W,2}^*$	Apparent contact angle for fine-scale roughness in Wenzel state
$\theta_{CB,2}^*$	Apparent contact angle for fine-scale roughness in Cassie-Baxter state
θ_{CB-W}^*	Apparent contact angle in ‘Cassie-Baxter-Wenzel’ state of wetting
θ_{CB-CB}^*	Apparent contact angle in ‘Cassie-Baxter-Cassie-Baxter’ state of wetting
θ_{nano}^*	Apparent contact angle of titanate nanowires
θ_{W-CB}^*	Apparent contact angle in ‘Wenzel-Cassie-Baxter’ state of wetting
θ_{W-W}^*	Apparent contact angle in ‘Wenzel-Wenzel’ state of wetting
ϑ	Angle of intrusion of liquid into structure
λ	Wavelength of the idealized sinusoidal roughness
λ_{max}	Maximum pore diameter
ν	Poisson’s ratio
ρ	Liquid density
ρ_f	Density of fibres
ϕ_{eff}	Effective porosity of the unit cell
ϕ_i	Porosity of particle cluster/finer scale self-similar unit
Φ	Roll-off angle
χ	Angle formed between the axis of fibres
ψ_{min}	Minimum local geometric angle
ψ	Local geometrical angle of the re-entrant curvature of fibre surface
ϖ	Width of the droplet
ω	Rise angle of frustoconical asperity
ω_1	Rise angle of the primary frustoconical asperity
ω_2	Rise angle of secondary features of frustoconical asperity
A	Amplitude of roughness (sinusoidal asperity)
A_o	Cross-sectional area of a representative volume element
A^*	Composite robustness factor
A_p	Total dimensionless pore area
A^+	Dimensionless total area of unit cell
a	Side of the square pillars

a_1	Side of the square pillars at coarse scale
a_2	Side of the square pillars at fine scale
$2B$	Width of the flattened portion of fibres after thermal bonding
b	Spacing between pillars
b_1	Spacing between pillars at coarse scale
b_2	Spacing between pillars at fine scale
$\bar{b}$	Mean distance between the centres of two adjacent fibres
$\bar{b}_b$	Mean length of overlapping fibre-fibre contact
$\bar{b}_l$	Mean free fibre length
$\bar{b}_j$	Mean distance between the centres of two adjacent fibres projected on the Z-direction
C	Fibre perimeter
D^*	Spacing ratio
$2D$	Average edge-to-edge distance between fibres
$2D'$	Edge-to-edge distance between flattened fibres after thermal bonding
D_f	Fractal dimension
D_m	Spatial dimension (Euclid geometry)
D_{fp}	Pore area fractal dimension
$2d_{cyl}$	Distance between edges of cylindrical fibres
d_{CNT}	Diameter of MWCNTs
d_e	Mean diameter of electrospun fibres
d_f	Fibre diameter
d_o	Minimum diameter of cluster particles
d^+	Ratio of diameter of micro-scale material to that of the nano-scale materials
dE	Free energy change
dx	Infinitesimal displacement of contact line
$f_{c,max}$	Maximum capillary force
f_{la}	Area fraction of liquid-air contact
f_{sl}	Area fraction of solid-liquid contact
$(f_{sl})_{cyl}$	Area fraction of cylindrical fibres in contact with the liquid droplet
$(f_{sl})_{micro}$	Area fraction of micro-scale nonwoven fibres in contact with liquid droplet

f_{sm}	Solid-liquid contact fraction at micro scale
f_{sn}	Solid-liquid contact fraction at nano scale
g	Acceleration due to gravity
g_{cyl}	Distance between the cylinder axes
H	Height of the pillars
H_1	Height of the pillars at coarse scale
H_2	Height of the pillars at fine scale
H^*	Robustness height
h_c	Height of droplet of volume V_c
h_{cyl}	Height of the cylindrical part of the droplet
h_1	Sagging height of droplet
h_2	Pore depth
I	Overall fibre orientation parameter
L	Length scale
L_c	Distance between adjacent particle clusters
l_f	Fibre length
l_{cap}	Capillary length
$M(L)$	Measure of a fractal object
m_d	Mass of the droplet
N	Total number of fibres
N_{ss}	Number of self-similar replicates
$N(\xi)$	Number of square boxes of side ξ covering the surface of a structure for the computation of fractal dimension.
n	Total number of fibre-fibre contacts
$\bar{n}$	Average number of contacts formed on an arbitrary fibre
$n_l/(n_l)_{micro}$	Ratio of the mean length of fibre-fibre contact to the length between the centres of two adjacent fibres (micro-scale)
$(n_l)_{nano}$	Ratio of the mean length of nanowire-nanowire contact to the length between the centres of two adjacent nanowires (nano-scale)
n_{meso}	Number of fibre-fibre contacts formed in the mesodomain
$\Delta P_{h,c}$	Critical hydrostatic pressure for complete intrusion
P^*	Dimensionless pressure difference
P_h	Pressure required for complete intrusion of water droplet

P_{CB-CB}^*	Dimensionless pressure difference across the liquid–air interface of SS-Ti-NMs exhibiting ‘Cassier-Baxter-Cassie-Baxter’ state of wetting
P_{ref}	Reference pressure
R_a	Surface radius of asperity
R_c	Cluster radius
R_{cyl}	Radius of cylindrical fibres
R'_f	Radius of the of the semi-circular region of the fibres
$(R_f)_{micro}$	Roughness factor of a nonwoven mat consisting of microfibres
$(R_f)_{CNT}$	Roughness factor of ensemble of MWCNTs
R_p	Radius of protuberances
r_f	Roughness factor
r_m	Roughness factor at micro scale
r_n	Roughness factor at nano scale
r	Similarity factor
T^*	Robustness angle
T_{eff}	Effective adhesive tension
T_o	Initial thickness of the nonwoven material
T_f	Final thickness of the nonwoven material
t	Thickness of nonwoven
V	Volume of fibrous assembly
V_c	Critical volume of water droplet that could be suspended on an asperity
V_{cyl}	Volume of cylindrical region of droplet above asperity
V_{cap}	Volume of droplet cap
V_{CNT}	Volume fraction of MWCNTs
V_{ann}	Annular volume of droplet
V_f	Fibre volume fraction
$(V_f)_{updated}$	Updated fibre volume fraction
V_{TiONW}	Volume fraction of titanate nanowires
W_{sl}	Work of adhesion
$2y$	Dimension of the unit cell

List of Acronyms

2D	Two-dimensional
3D	Three-dimensional
ACA	Advancing contact angle
CAH	Contact angle hysteresis
CB	Cassie-Baxter
CB-CB	Cassie-Baxter-Cassie-Baxter
CB-W	Cassie-Baxter-Wenzel
CF	Carboxyfluorescein
CNT	Carbon nanotubes
CTAn	CT-analyser
DMF	Dimethyl formamide
EDX	Energy Dispersive X-ray analysis
EMI	Electromagnetic
F-CNPs	Fluorinated chained nanoparticles
iCVD	Initiated chemical vapour deposition
LBL	Layer-by-layer
MD	Membrane desalination
MIL	Mean intercept length
MNWF	Microfibre nylon nonwoven fabric
MWCNTs	Multi-walled carbon nanotubes
NM	Nanostructured material
PAA	Poly (acrylic acid)
PAN	Polyacrylonirile
PET	Polyester
PDA	Polydopamine
PDMS	Poly(dimethylsiloxane)
PHBV	Poly(hydroxybutyrate-co-hydroxyvalerate)
PLA	Poly (lactic acid)
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene

PVDF	Polyvinylidene fluoride
RCA	Receding contact angle
RVE	Representative volume element
SEM	Scanning electron microscope/microscopy
SS-CNT-NMs	Self-similar nonwoven-carbon-nanotube nanostructured materials
SS-Ti-NMs	Self-similar nonwoven-titanate nanostructured materials
TCL	Three-phase contact line
TEM	Transmission electron microscopy
TiONWs	Hydrophobized titanate nanowires
TPU	Thermoplastic polyethylene
UV	Ultraviolet irradiation
VOI	Volume of interest
X-ray microCT	X-ray micro-computed tomography
ZnO	Zinc oxide