Fabrication of Polyamide 6-based CFRP with Water Resistance via T-RTM Process and Fluorinated Polydopamine Coating

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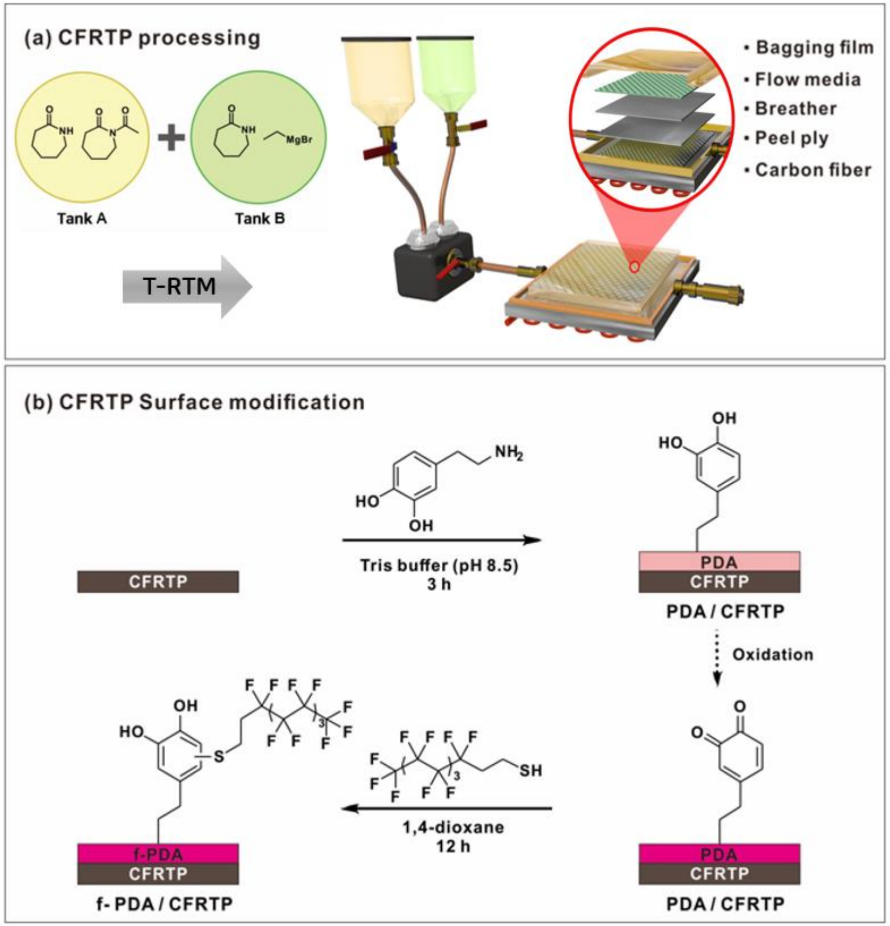

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Introduction : Polyamide 6 (PA 6)-based Carbon Fiber Reinforced Thermoplastic (CFRTP)

Sustainable structural material owing to lightweight property and recyclability

https://steamdaily.com/top-ten-awesome-uses-of-carbon-fibre-2/

Advantages of PA 6-based CFRTP (compared to steel)

- Lightweight and anti-corrosion
- Superior specific strength and elasticity
- Short processing time (heating and cooling)

Advantages of PA 6-based CFRTP (compared to CFRP)

- High impact resistance
- Weldability and recyclability
- Low adhesion to mold and long shelf life

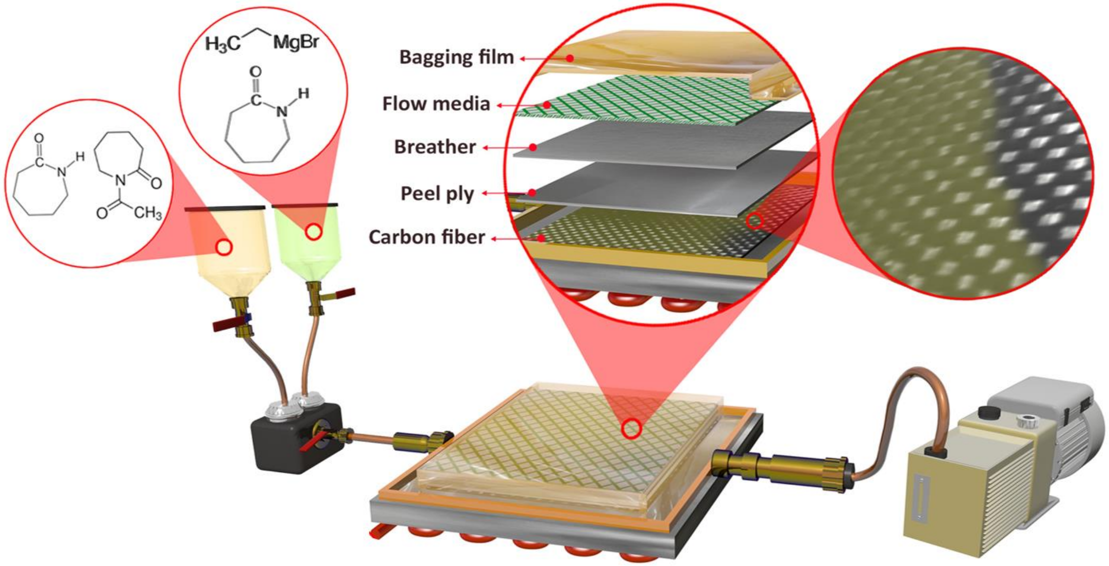
[Limitations for industrial and exterior application]

① **High melt viscosity of PA 6 :** difficult to impregnate the resin into to fiber

② **Water absorption and high surface energy :** deterioration of mechanical properties

Concept 1 - T-RTM process : Liquid Molding Process for PA 6-based CFRTP

Integrated reactive process of mixing, injection, impregnation, and polymerization



Thermoplastic reactive resin transfer molding

- Tank 1 : monomer & activator
- Tank 2 : monomer & Grignard catalyst
- Anionic polymerization occurs in the preform

T-RTM's advantages

- Low processing temperature (150 ℃)
- Low resin viscosity (0.01 Pa·s)
- Inexpensive material cost (ε-caprolactam)

Extremely low viscosity of resin : 1/100 of epoxy, 1/160,000 of PA 6

Advantageous process for large production of PA 6-based CFRTP

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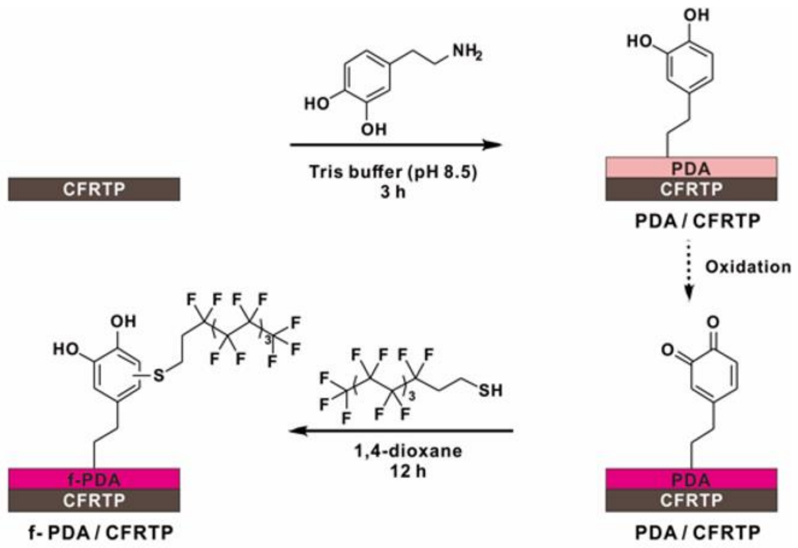
Concept 2 - Polydopamine Chemistry : Mussel-inspired Surface Treatment

Coating method with strong adhesive force by covalent and noncovalent interactions

https://www.snexplores.org/article/mimicking-mussels-muscle-for-underwater-superglue-better-stitches



Polydopamine (PDA) coating

- Robust and reliable surface treatment
- Suitable for large and complex shaped products
- Spherical aggregation (Cassie-Baxter state)

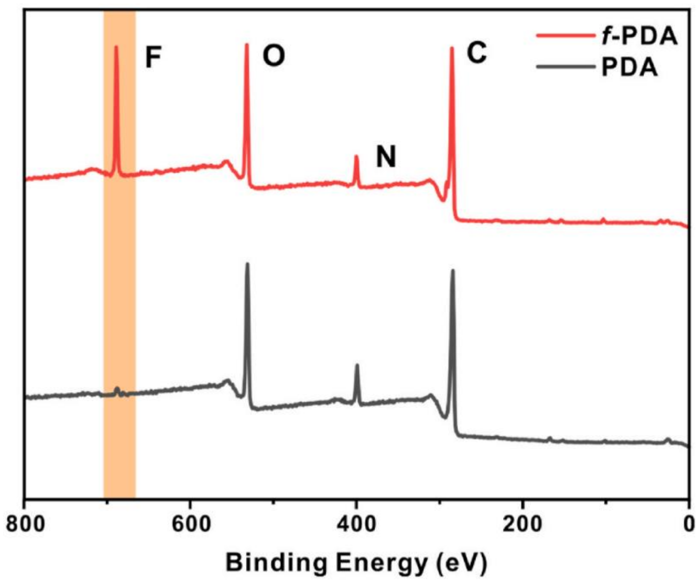
Fluorinated Polydopamine (f-PDA) coating

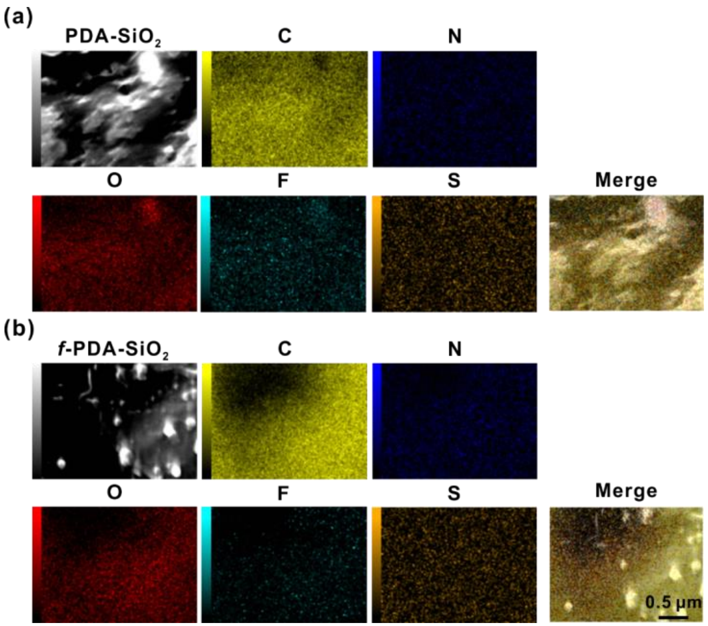
- Michael type addition reaction (click chemistry)
- Low surface energy and wettability
- Anti-fouling and water resistance performance

Overcome the disadvantages of PA 6-based CFRTP by T-RTM and f-PDA

Result and discussion : Surface Element Analysis of f-PDA : XPS and EDS

PDA was modified with fluoroalkyl chain by Michael-type addition reaction



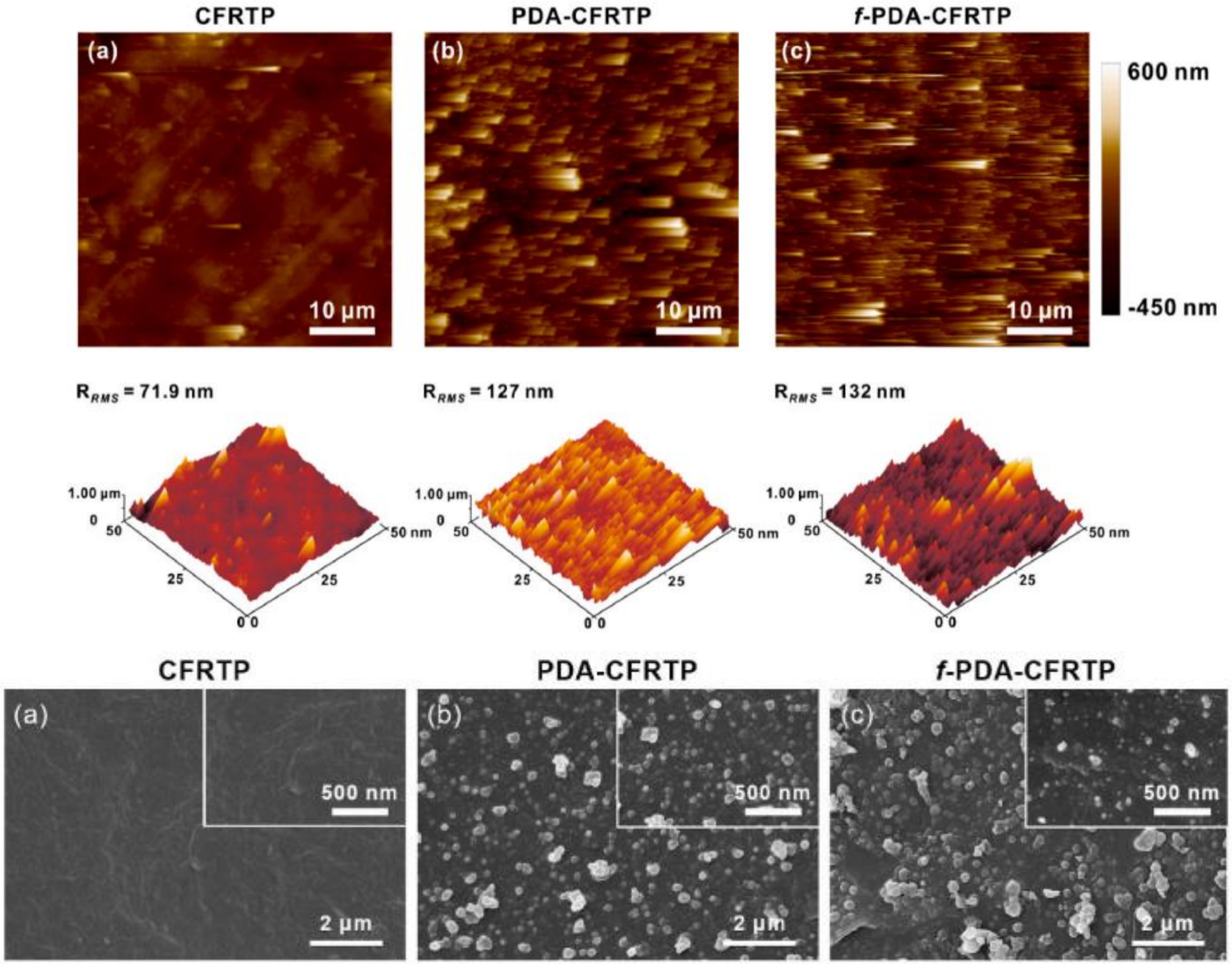


f-PDA surface consisted of C (67.4 at%), O (20.6 at%), N (6.5 at%), and F (4.9 at%)

Fluorine's low surface energy : hydrophobicity and low wettability

Result and discussion : Surface Morphology Analysis of f-PDA : AFM and SEM

PDA's roughness was maintained in the f-PDA : Cassie-Baxter state



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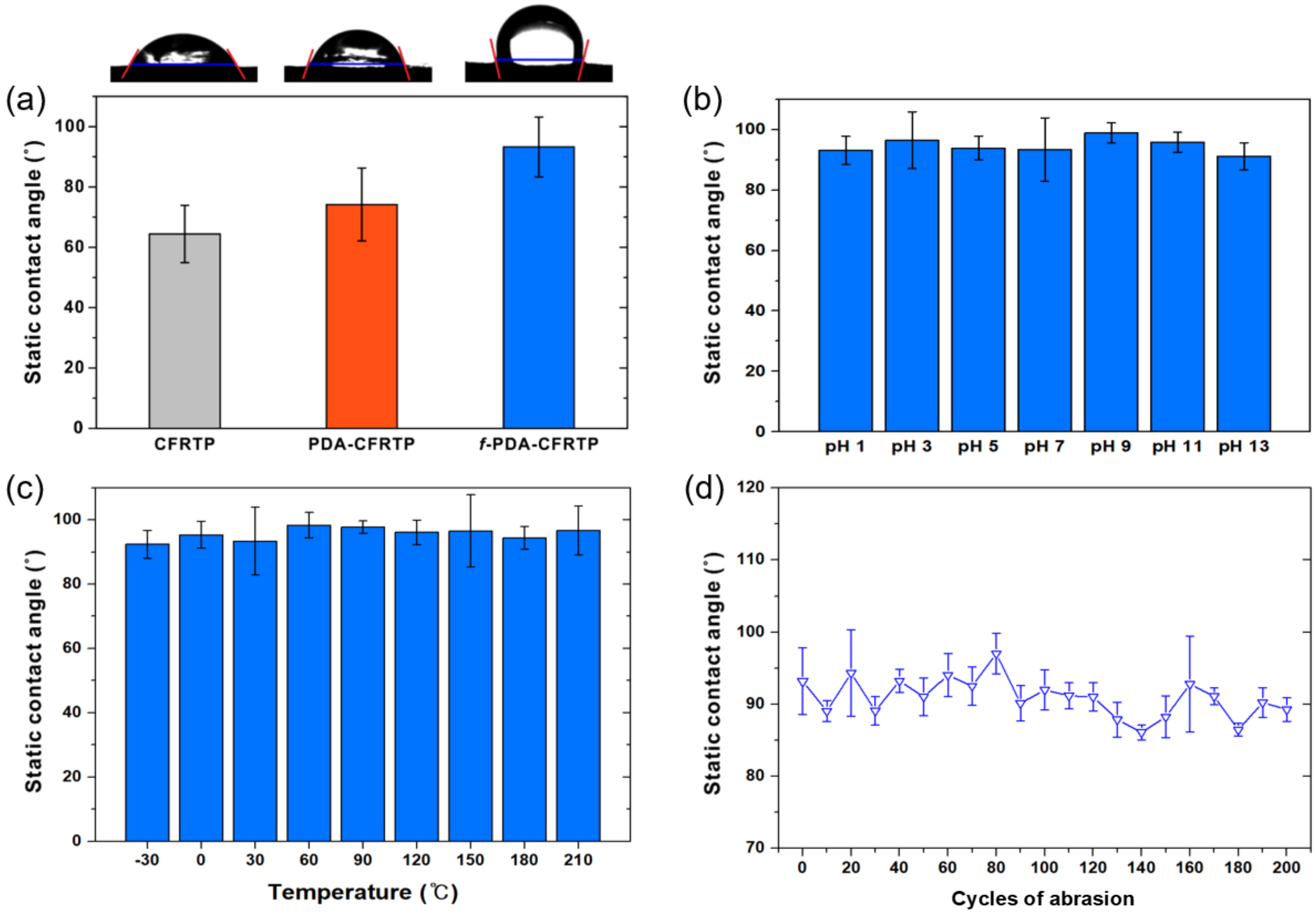
Result and discussion : Water Resistance and Durability Test of f-PDA-CFRTP

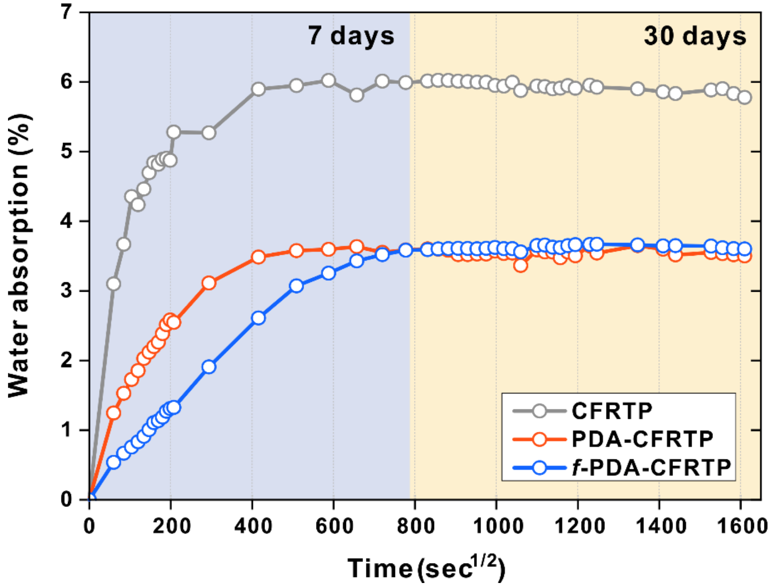
Chemical, thermal, and mechanical stability of f-PDA coating



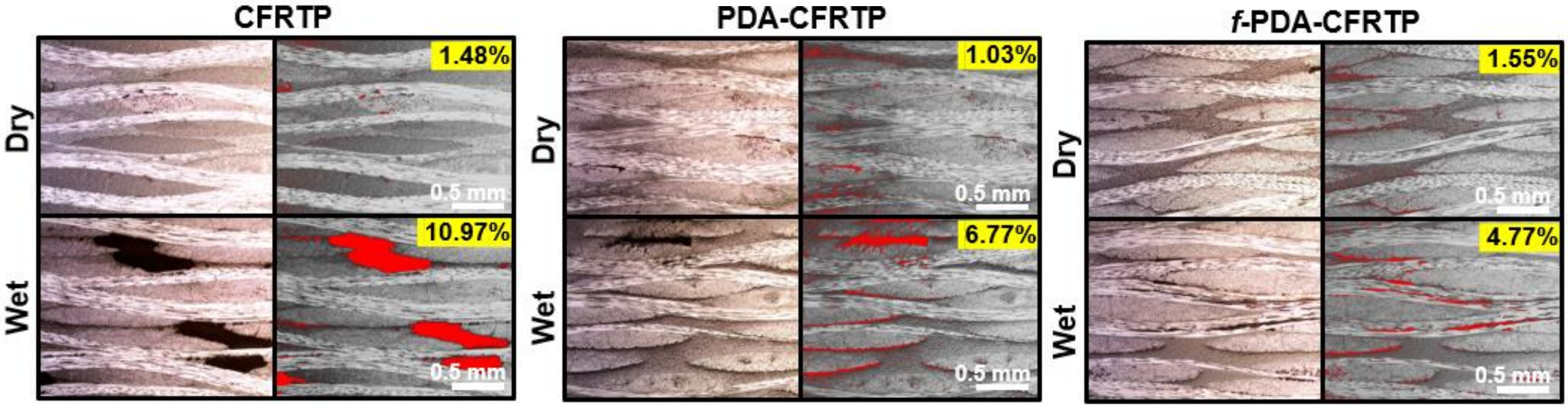
f-PDA-CFRTP is durable enough to be applied as exterior materials

Result and Discussion : Water Absorption and Void Contents after Hydrolysis

Water absorption was reduced by 42% for 30 days by introduction of f-PDA



- CFRTP → 60 ℃ D.I water for 30 days : Fickian diffusion behavior
  → amorphous region of PA 6 & interface of fiber and matrix
- PDA coating → physically barrier effect
- f-PDA coating → barrier effect + low wettability & hydrophobicity



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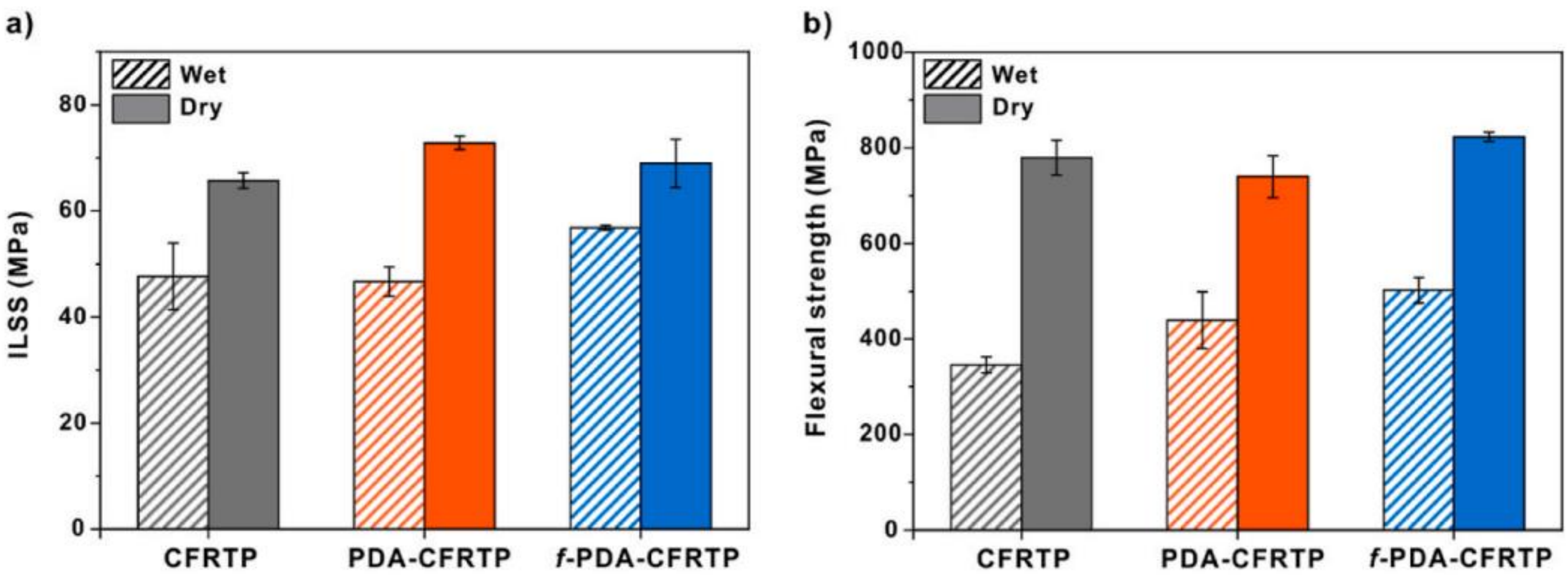
Result and discussion : Mechanical Properties of f-PDA-CFRTP : ILSS and Flexural Test

Mechanical properties of composites at dry and wet states



Flexural strength : matrix-based property : improved 31%

ILSS : interfacial bonding between matrix and fiber : improved 16%

Deterioration of mechanical properties by water was alleviated by f-PDA

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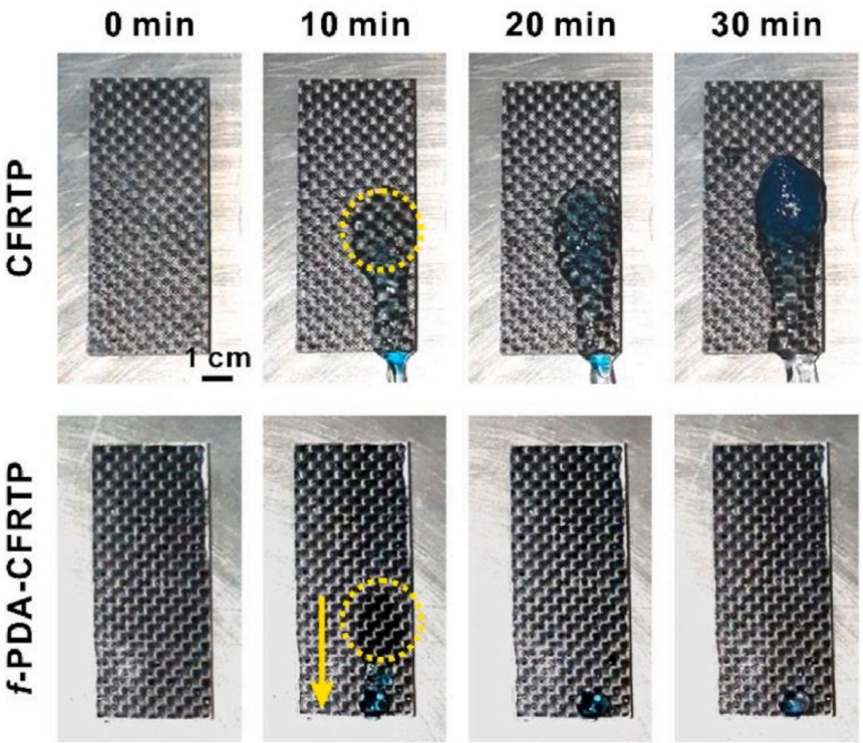
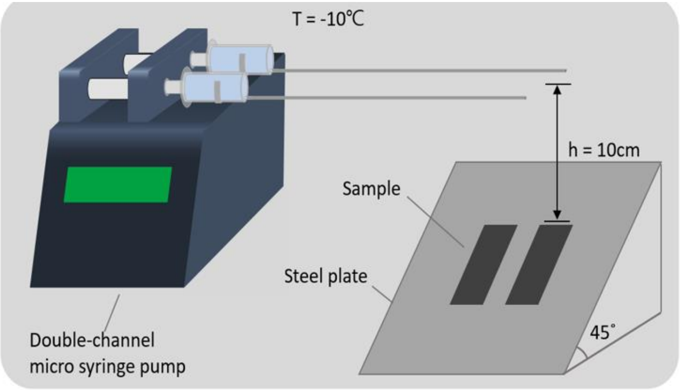
Result and discussion : Anti-Icing Test f-PDA-CFRTP : Surface Energy Reduction

Surface energy was reduced by 49% : anti-icing, anti-fouling, and hydrophobicity



Substrates	Contact angles (°)		Surface energies (dyne/cm^2)		
	θ_{water}	$\theta_{diiodomethane}$	γ^D	γ^P	γ
CFRTP	64.4	30.0	37.1	10.7	47.8
PDA-CFRTP	73.2	32.4	38.3	6.1	44.4
f-PDA-CFRTP	90.1	69.6	19.8	4.6	24.4



① Chemical term : surface energy was reduced 49% (fluorine effect)

② Physical term : friction between solid and liquid droplet (PDA effect)

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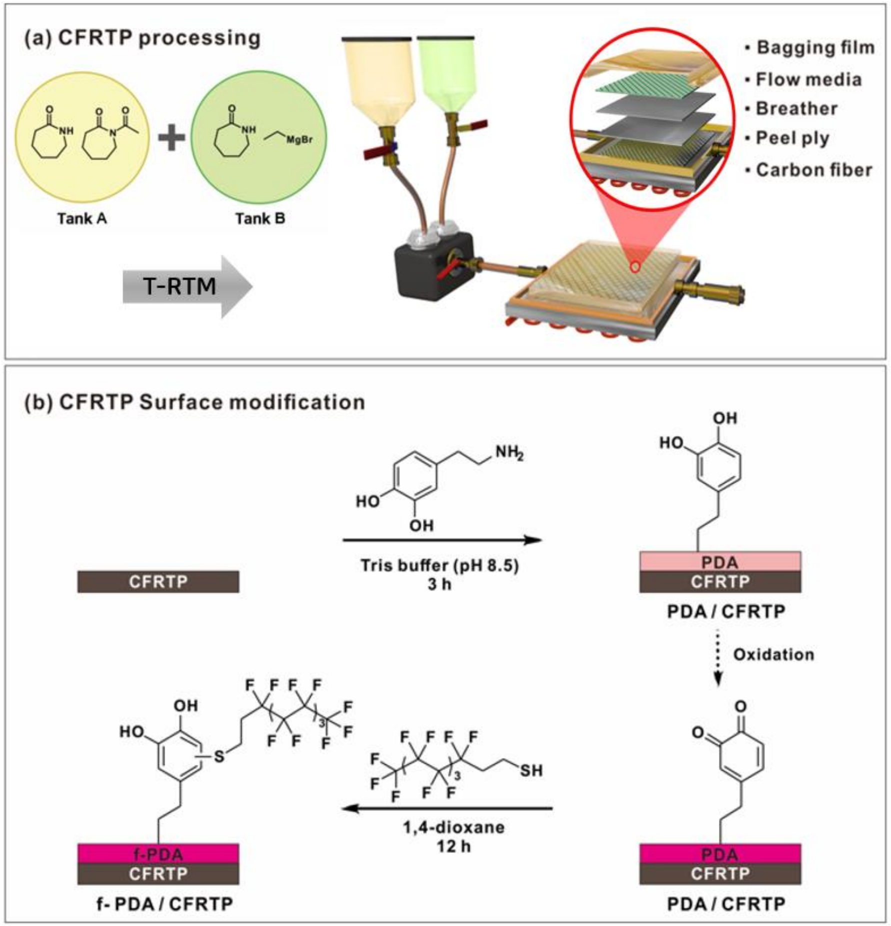
Conclusion : T-RTM and f-PDA Coating for PA 6-based CFRTP

Applying PA 6-based CFRTP as various external component in humid environments



Eco-friendly thermoplastic composite by T-RTM process

- 1/160,000 of viscosity

Water absorption and surface energy

- f-PDA coating
- Water absorption was reduced by 42%
- Surface energy was reduced by 49%

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Thank you for your attention

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Fabrication of carbon fiber/polyamide 6 composites with water resistance and anti-icing performance using a superhydrophobic fluorinated-polydopamine coating

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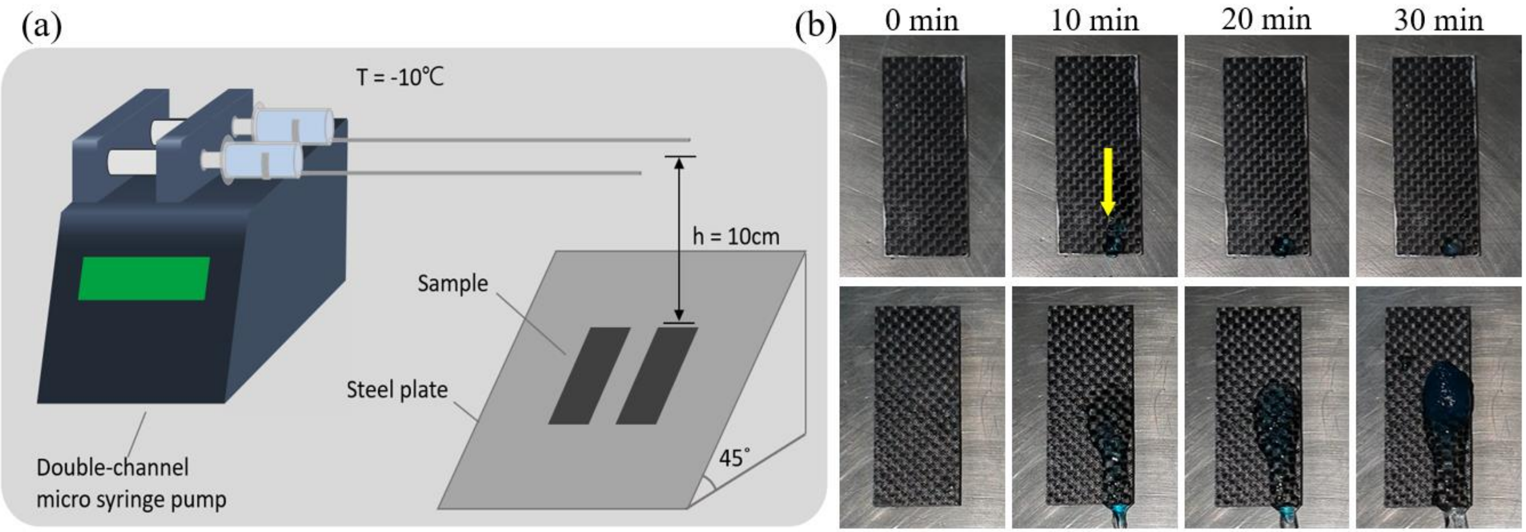
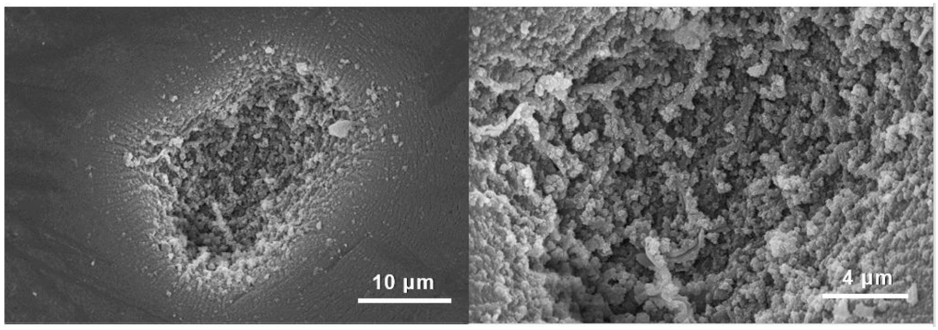
Supporting information

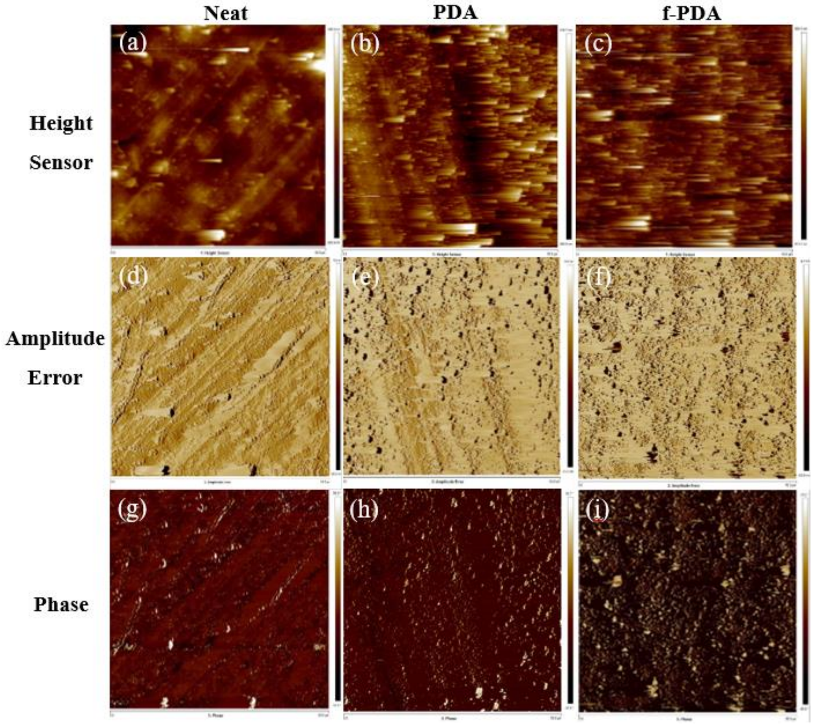
Anti-icing test

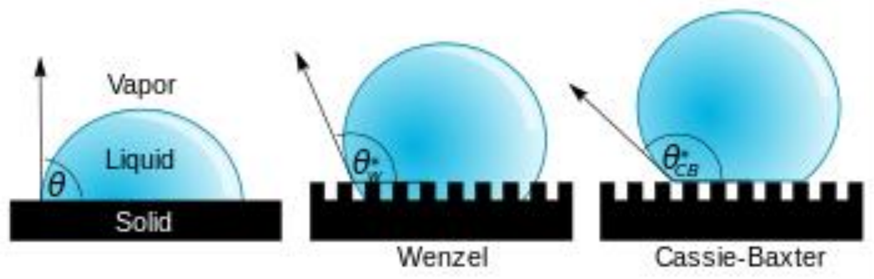




Supporting information

AFM data (amplitude error, phase), Cassie-Baxter state





https://en.wikipedia.org/wiki/Cassie%27s_law

Supporting information

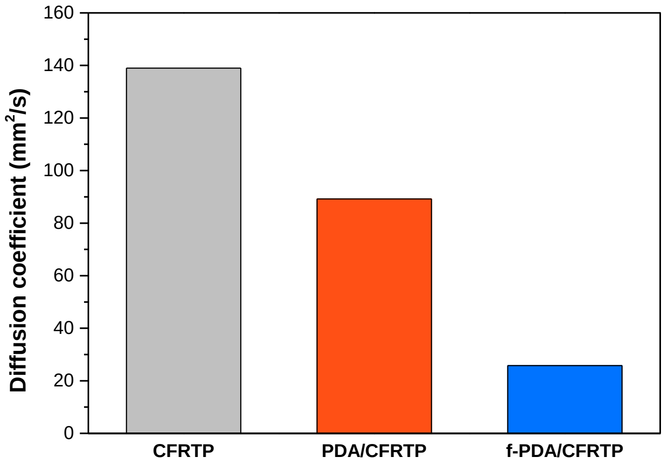
Owens-Wendt equation, water absorption, and diffusion coefficient of water

$$\gamma_{SL} = \gamma_{SG} + \gamma_{LG} - 2\left(\gamma_{SG}^{d} \bullet \gamma_{LG}^{d}\right)^{½} - 2\left(\gamma_{SG}^{p} \bullet \gamma_{LG}^{p}\right)^{½},$$

$$\gamma_{LG}(1 + \cos\theta) = 2\left(\gamma_{SG}^{d} \bullet \gamma_{LG}^{d}\right)^{½} + 2\left(\gamma_{SG}^{p} \bullet \gamma_{LG}^{p}\right)^{½},$$

$$\gamma_{SG} = \gamma_{SG}^{d} + \gamma_{SG}^{p},$$

$$Water\ absorption\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \text{ x } 100$$



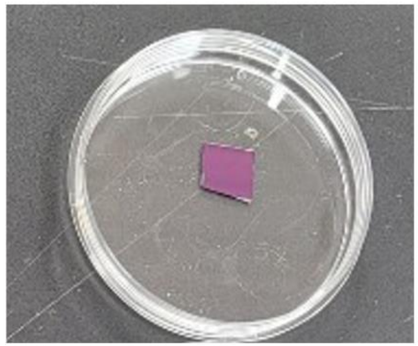
$$D_{water} = \pi\left(\frac{h}{4M_m}\right)^2\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2$$

Y. Ma, S. Jin, T. Yokozeki, M. Ueda, Y. Yang, E.A. Elbadry, H. Hamada, T. Sugahara, Effect of hot water on the mechanical performance of unidirectional carbon fiber-reinforced nylon 6 composites, Compos. Sci. Technol. 200 (2020), 108426, https://doi.org/10.1016/j.compscitech.2020.108426.

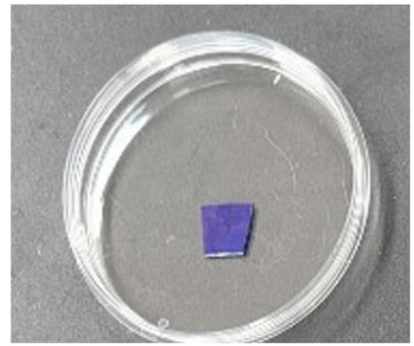
Supporting information

Color change and thickness optimization (ellipsometry)

Bare Si wafer



PDA-coated surface



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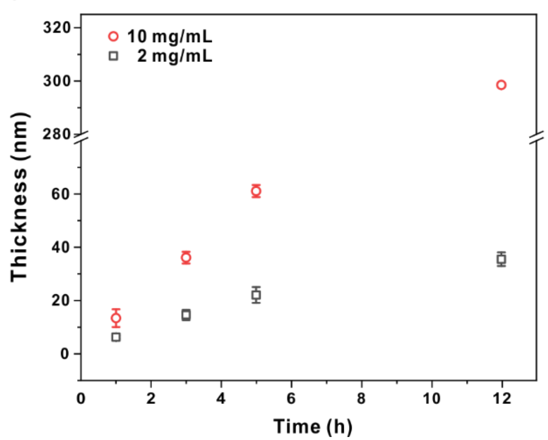

(b)