Novel double-networked cellulose based shape memory polymer composites

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2. Background

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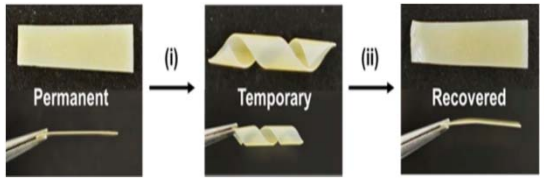
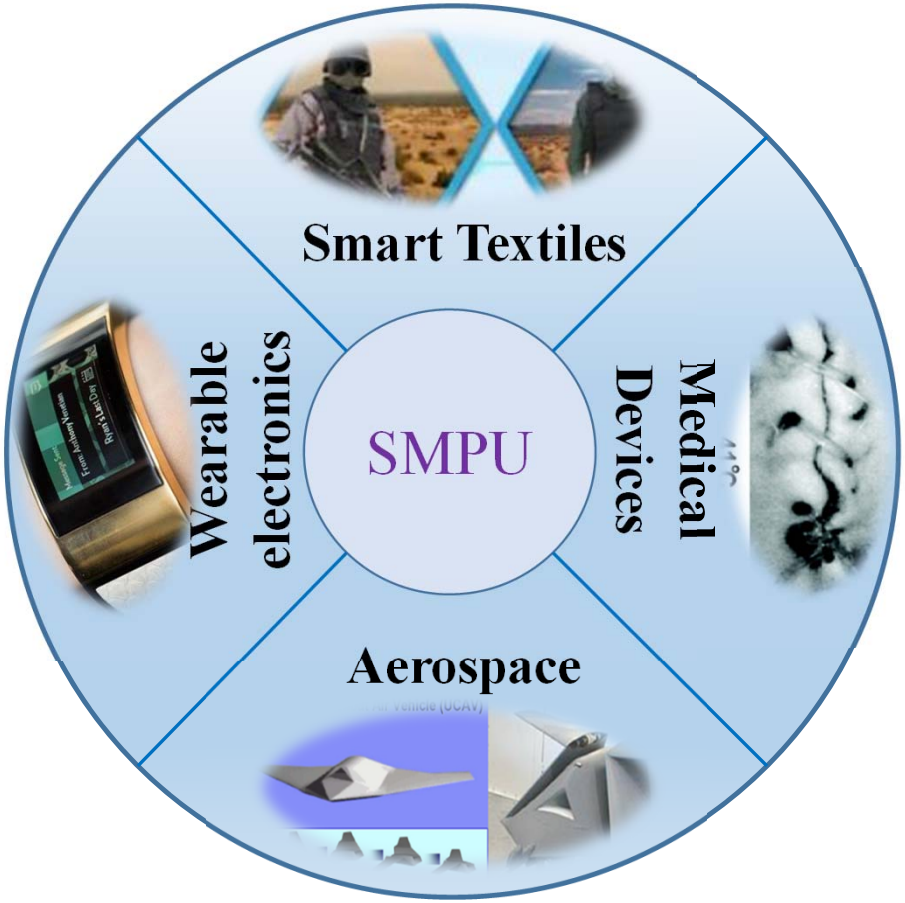
1. Introduction

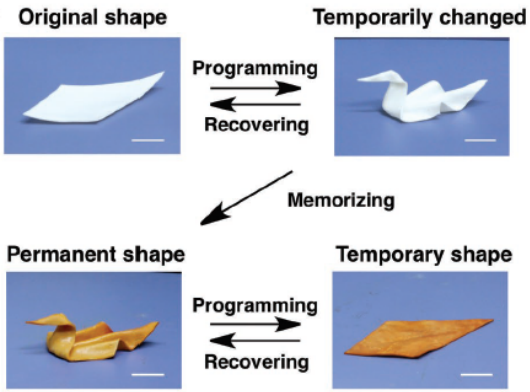
Large Strain



Smart Structure



Stimulus Responsive



Processable

2. Background and Purpose

SMPU

Poor mechanical properties

Low shape recovery capacity

Single thermal stimulus

How to solve these problems ?

Approach: Polymer composites

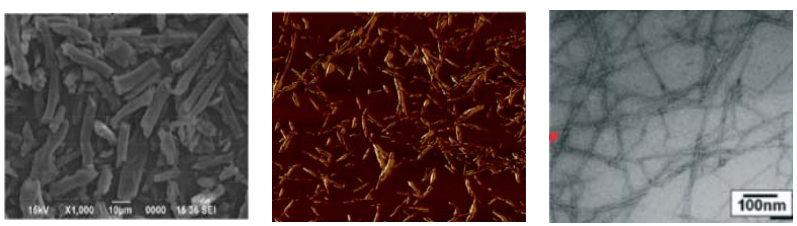
- ***Carbon nanotubes***
- ***Cellulose***
- ***Chitin***
- ***Clay***
- ***……et al***

2. Background and Purpose

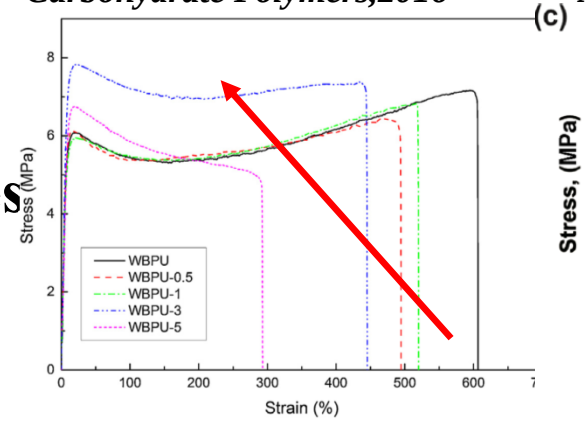
Cellulose

- ✓ Excellent mechanical properties
- ✓ Surface active group
- ✓ Biodegradable
- ✓ Low cost

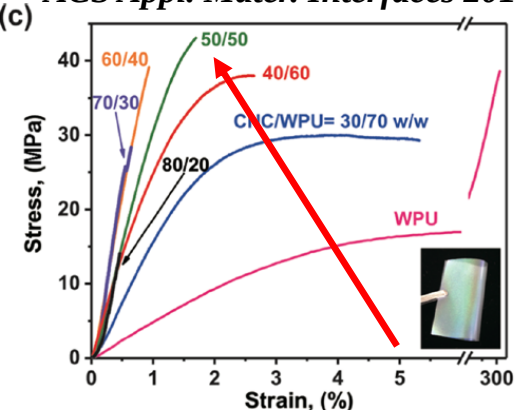
Idea reinforcement



Carbohydrate Polymers,2016



ACS Appl. Mater. Interfaces 2018



Composites Science and Technology, 2014

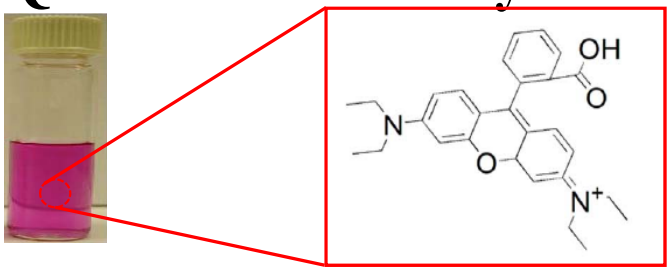
Sample	E (MPa)	σ_y (MPa)	σ_{max} (MPa)	ε (%)
STPU17	238.8 ± 6.7	10.3 ± 0.8	26.5 ± 2.3	762 ± 42
STPU17/CNC-0.25	264.4 ± 5.6	10.9 ± 0.8	24.0 ± 2.1	690 ± 38
STPU17/CNC-0.5	272.7 ± 7.2	11.3 ± 0.7	19.3 ± 1.9	591 ± 39
STPU17/CNC-0.75	297.4 ± 6.7	12.5 ± 0.9	17.3 ± 2.2	551 ± 24
STPU17/CNC-1	321.6 ± 8.3	14.1 ± 1.0	15.7 ± 2.0	430 ± 20
STPU17/CNC-2	328.4 ± 11.2	15.4 ± 1.2	14.9 ± 1.9	352 ± 21

Strength and modulus increase, toughness decrease

2. Background and Purpose

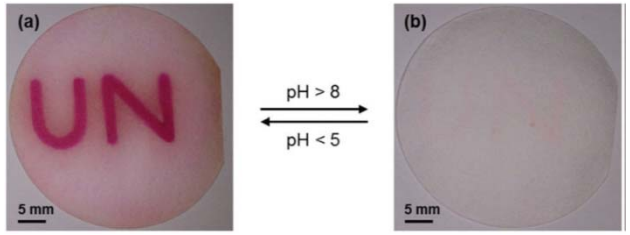
Rhodamine B

- ✓ Good stability
- ✓ Excellent optical properties
- ✓ Low cost
- ✓ Quantum efficiency

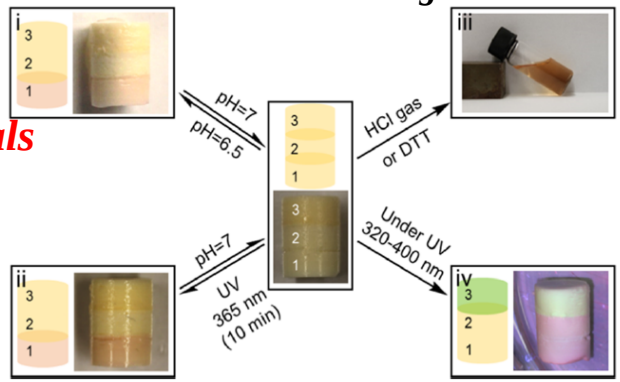


Photochromic materials

J. Mater. Chem. C, 2017



ACS Sustainable Chem. Eng. 2017

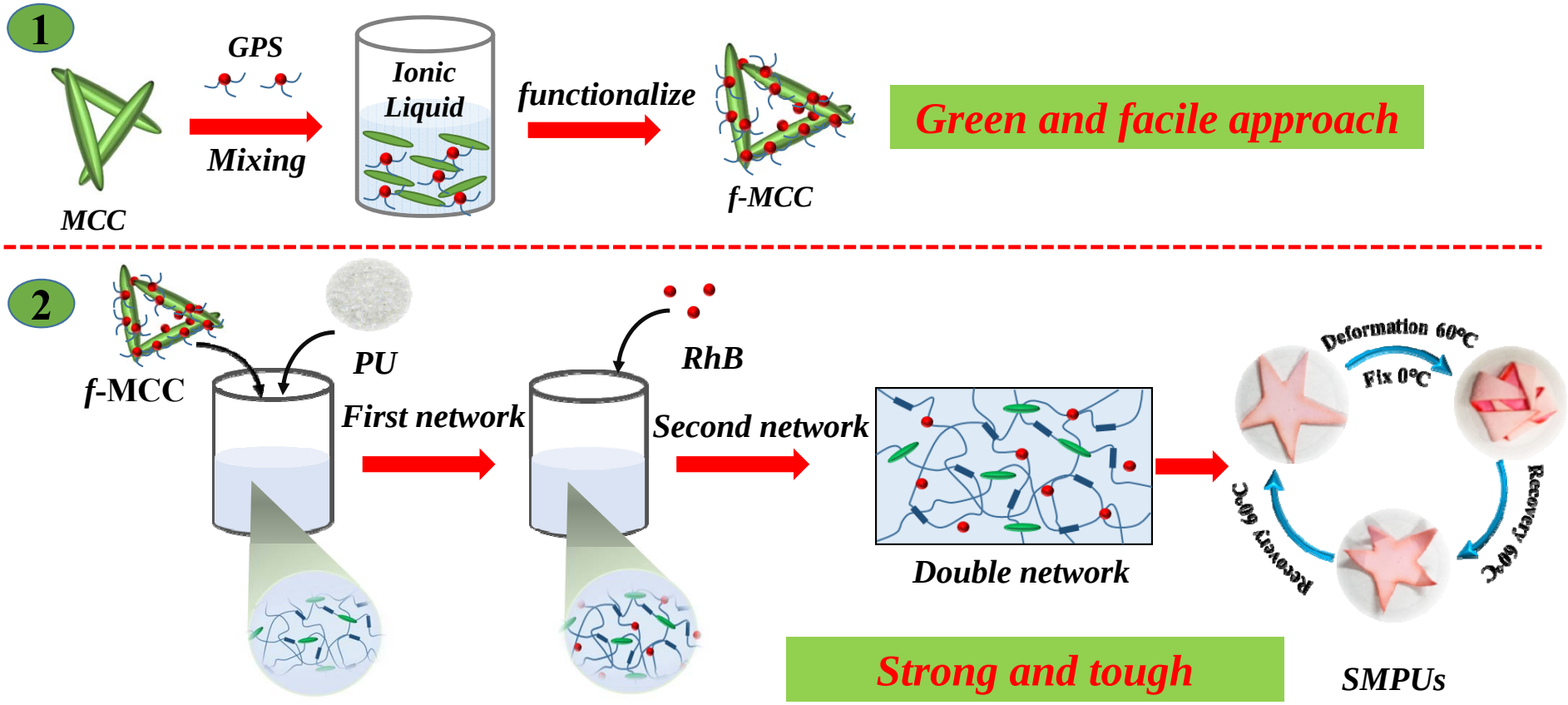


Structure modifier

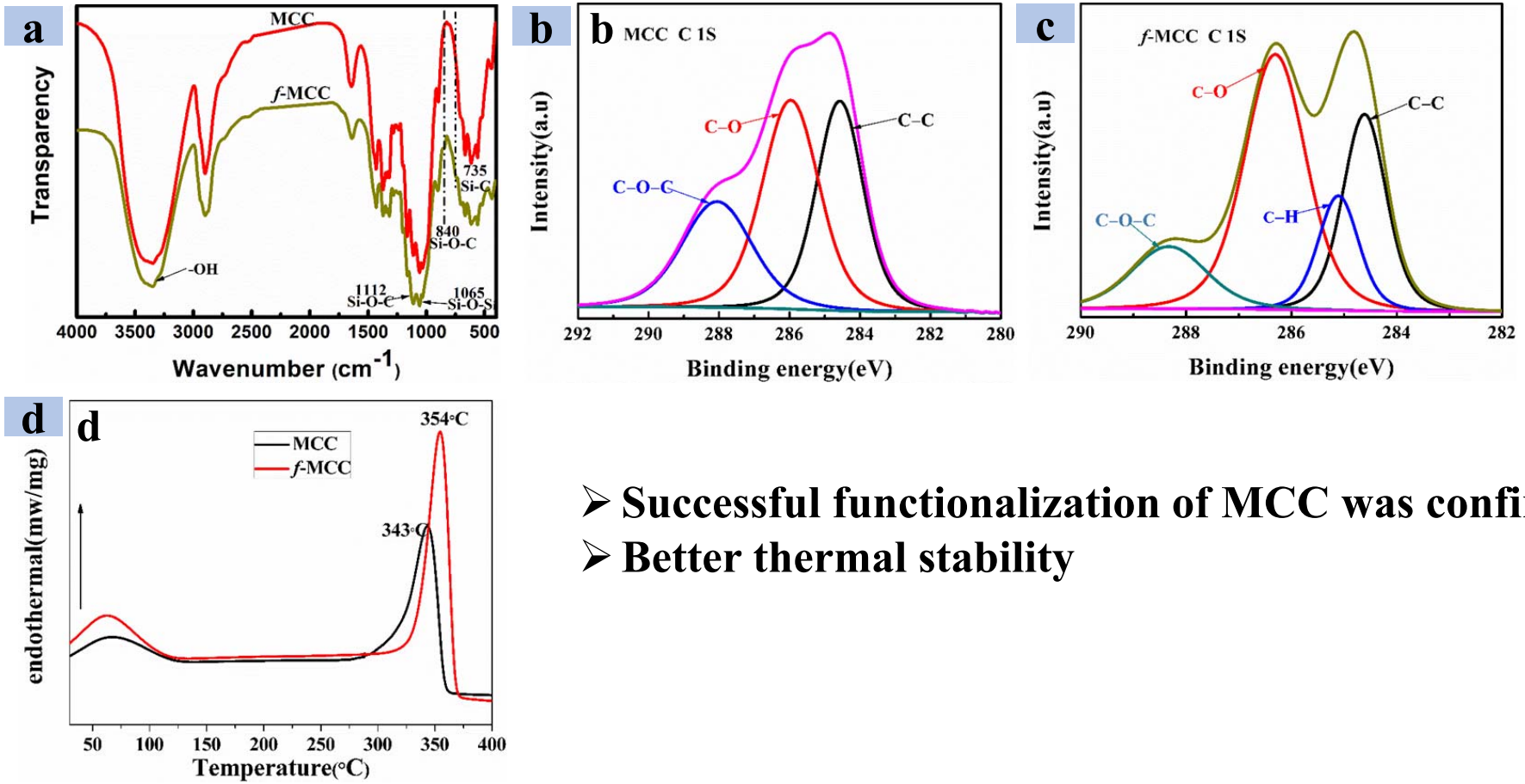
?

3. Experiment

3.1 Design multifunctional polyurethane composites

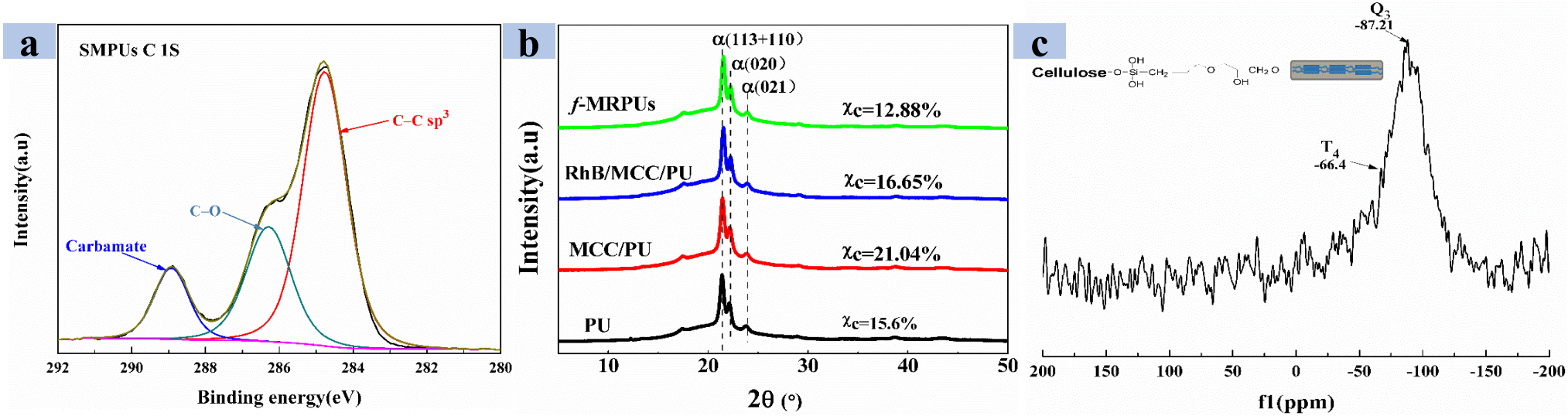


3.2 Chemical structure of functionalized MCC



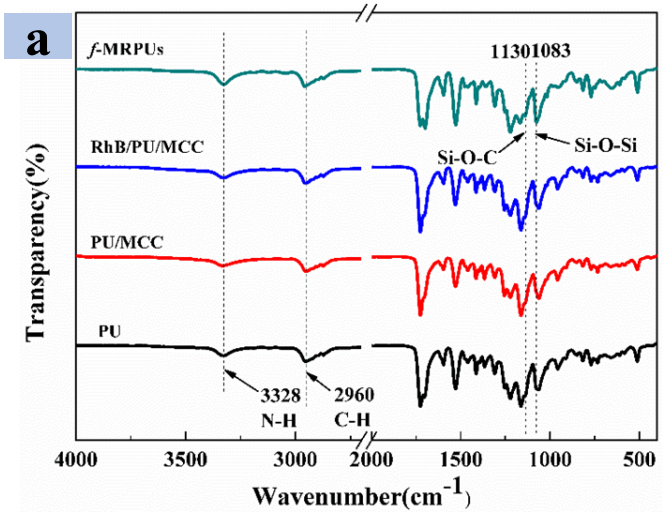
- **Successful functionalization of MCC was confirmed**
- **Better thermal stability**

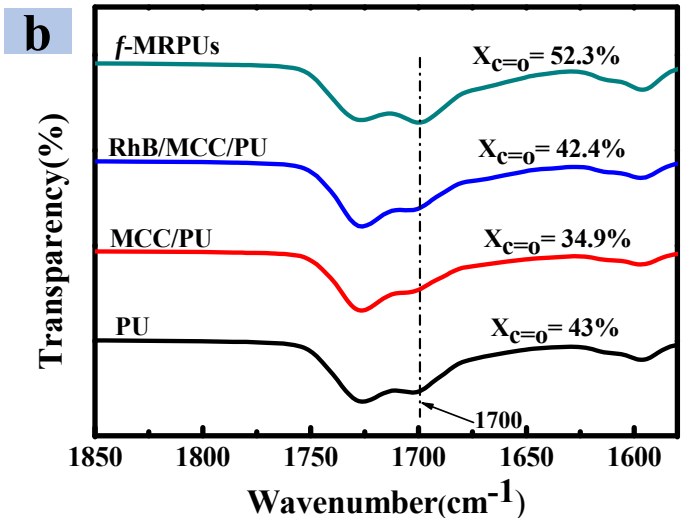
3.2 Chemical structure of SMPUs



- Xc of *f*-MRPUs decreased dramatically
- First network confirmed by NMR

3.3 Chemical structure of Shape memory polyurethane composites





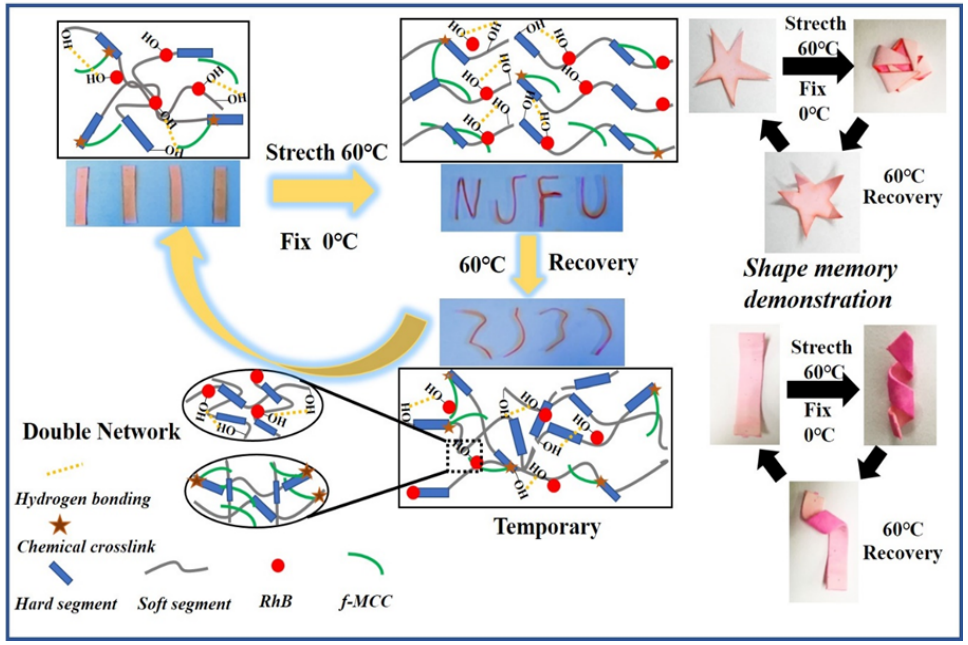
The fractions of hydrogen bonded C=O ($X_{C=O}$) are given :

$$X_{C=O} = \frac{S_b}{S_b + S_f}$$

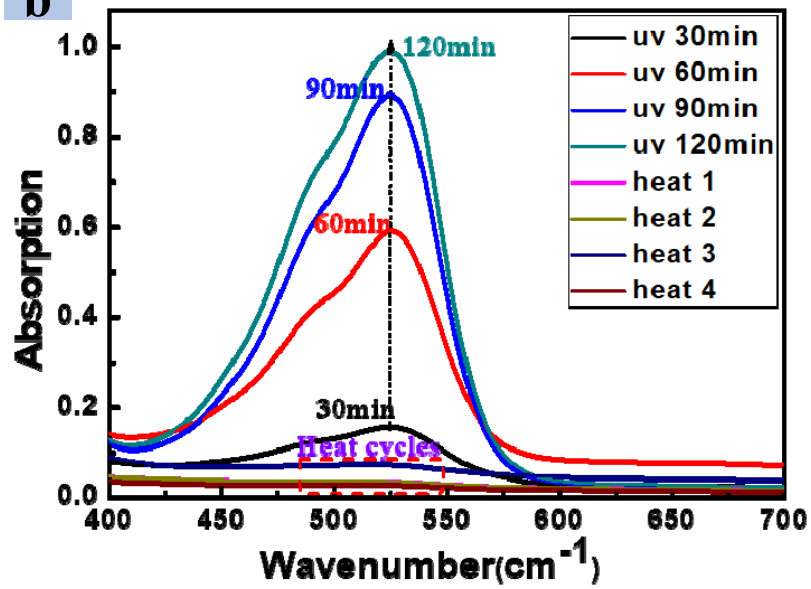
- Strengthening hydrogen bonding was observed
- Second flexible network formed

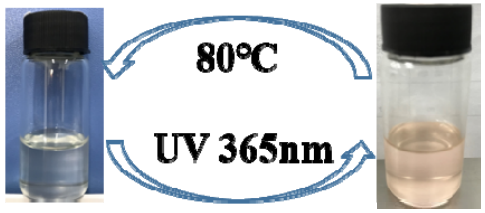
3.4 Multi-functionalities of SMPUs

a



b





- ➢ **Excellent thermal shape memory property**
- ➢ **UV-Heat responsive photochromic property**

3.5 Shape memory property of SMPUs

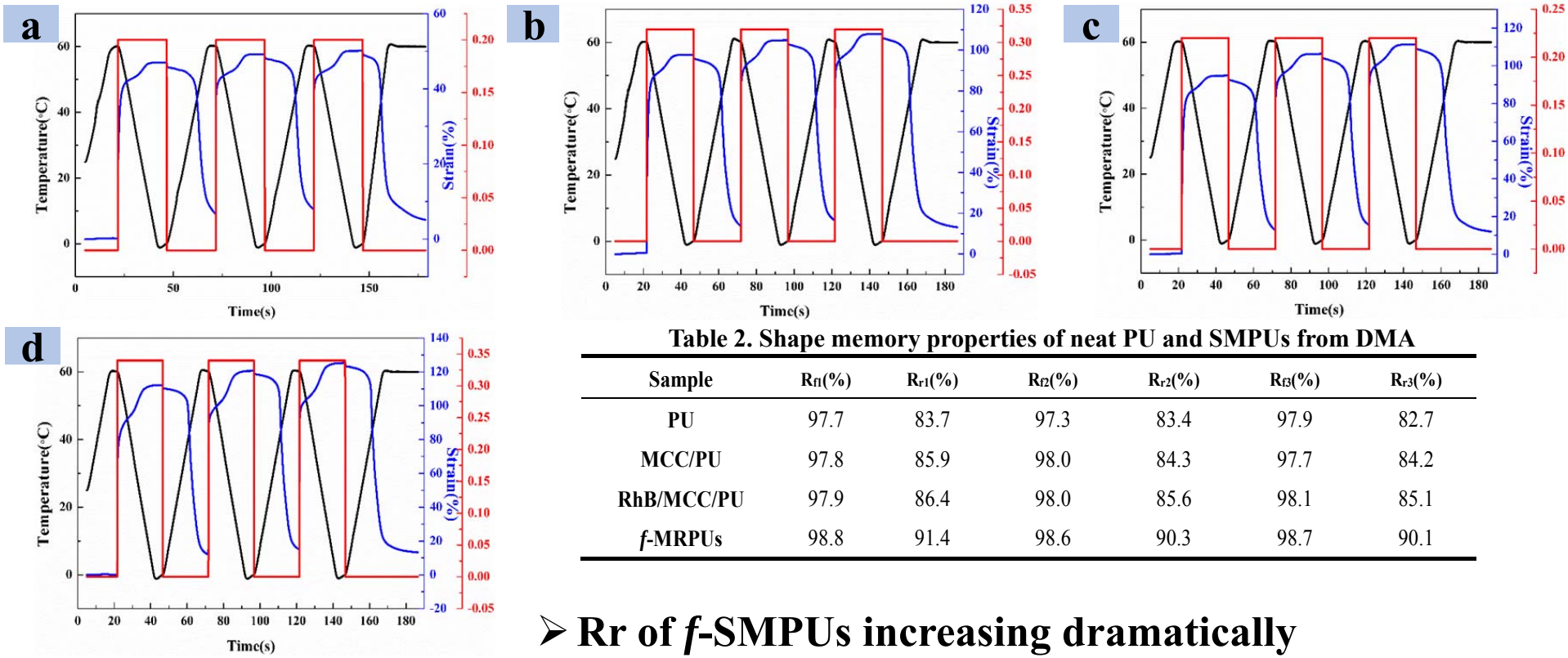


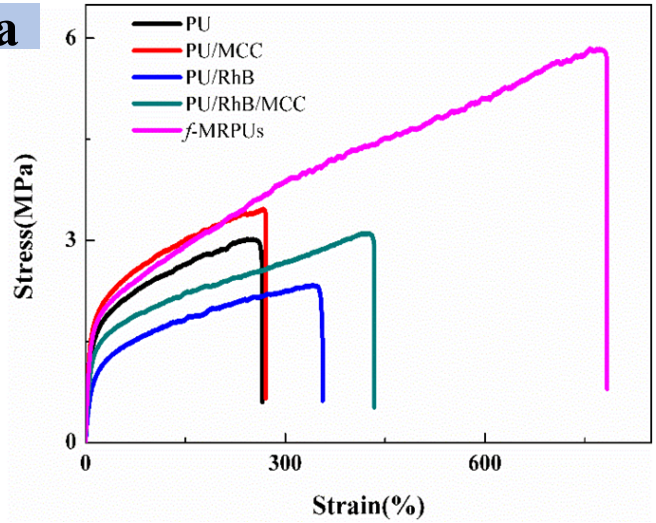
Table 2. Shape memory properties of neat PU and SMPUs from DMA

Sample	R_{f1}(%)	R_{r1}(%)	R_{f2}(%)	R_{r2}(%)	R_{f3}(%)	R_{r3}(%)
PU	97.7	83.7	97.3	83.4	97.9	82.7
MCC/PU	97.8	85.9	98.0	84.3	97.7	84.2
RhB/MCC/PU	97.9	86.4	98.0	85.6	98.1	85.1
f-MRPUs	98.8	91.4	98.6	90.3	98.7	90.1

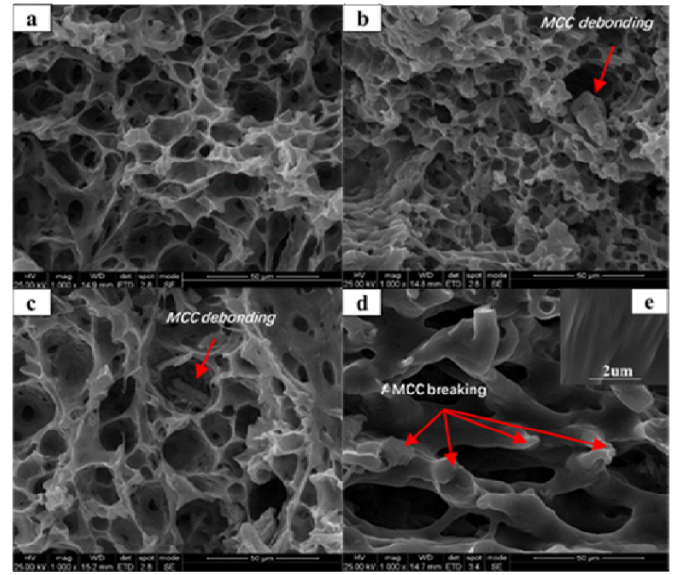
- **Rr of *f*-SMPUs increasing dramatically**
- **Double network improving shape memory ability**

3.6 Mechanical property of SMPUs

a



b

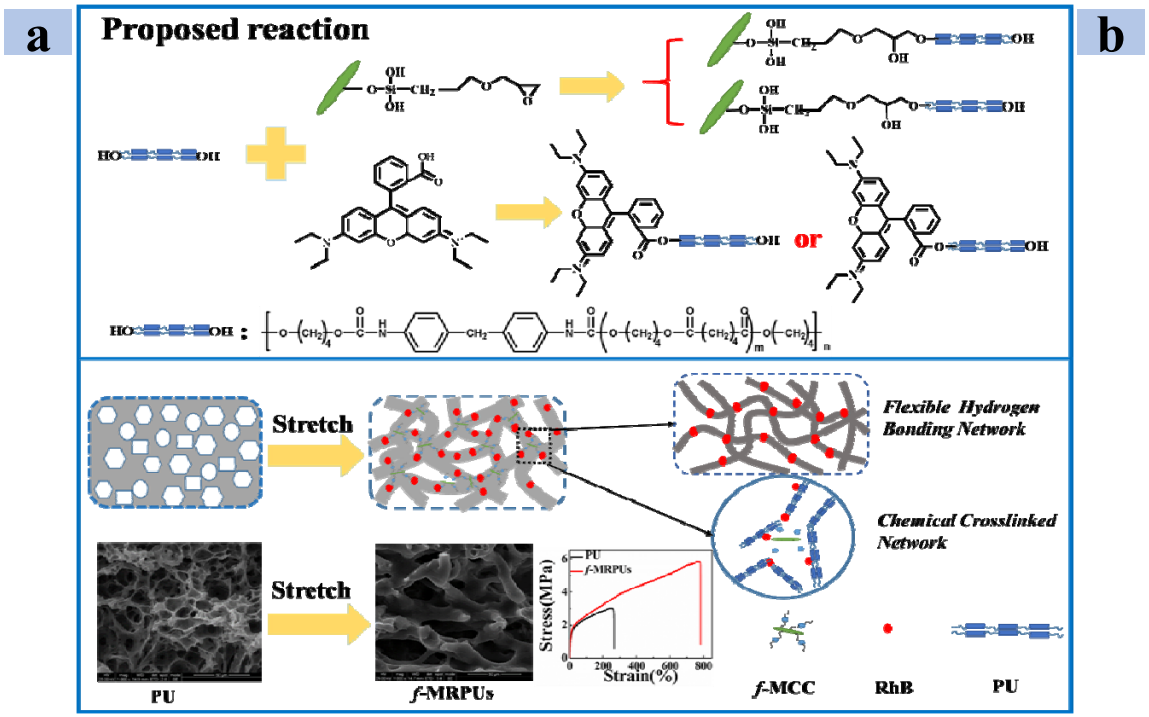


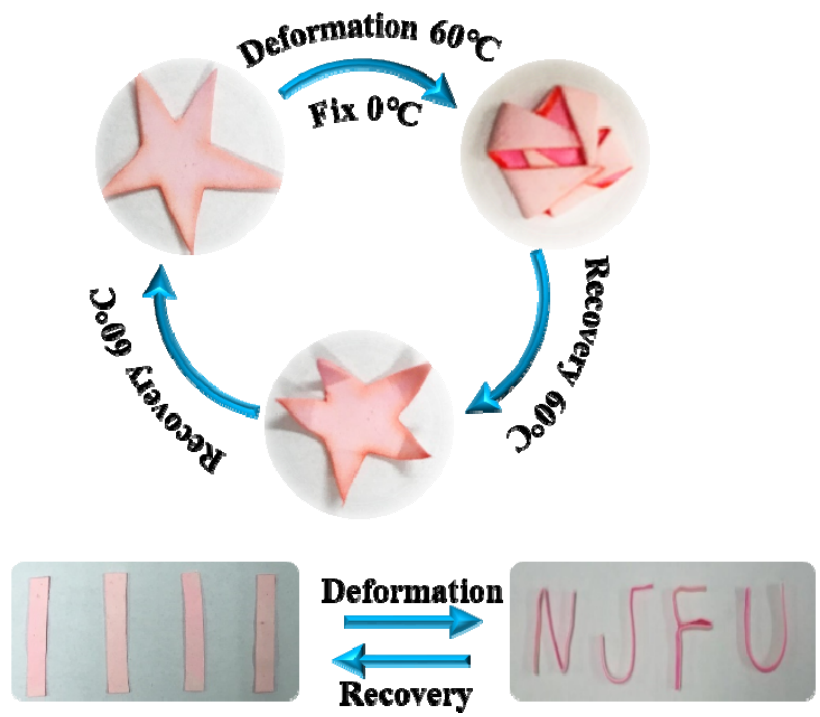
Mechanical properties of neat PU and PU composites

Sample	σ (MPa)	E (MPa)	ε_{max} (%)
PU	3.0±0.2	25.9±2.6	267.3±26.2
MCC/PU	3.4±0.1	31.6±2.1	286.1±9.3
RhB/MCC//PU	3.1±0.1	19.7±1.3	413.2±34.3
f-MCC/PU	3.9±0.2	34.8±1.6	202.1±23.7
f-MRPUs	5.8±0.3	19.1±1.3	706.5±22.9

- **Simultaneous reinforcing and toughening in *f*-MRPUs**

3.7 Proposed mechanism of Double network





Cai C, et al.. Journal of Materials Chemistry A, 2018, 6, 17457-17472.

- ***f*-MCC formed rigid chemically crosslinked network**
- **RhB was responsive for flexible network**

4. Conclusion

- **Develop a green approach for functionalization of MCC**

- **Novel double-networked microstructures were achieved by *f*-MCC , RhB and PU**

- **2-fold and 3-fold increases in strength and strain-to-failure as well as dramatically improved shape memory ability were achieved, when compared with the unmodified PU.**

- **Under the external stimuli of UV light and heating, the SMPU composites still showed outstanding photochromic properties and color reversibility**

Thank you

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