Metal coordination reinforced polyacrylamide-based physical hydrogels composited with carboxylated cellulose derivatives

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Introduction

Hydrogels: Soft and wet materials with polymer networks containing water.

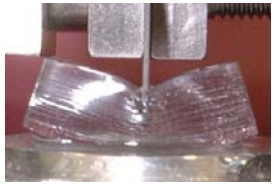
Traditional hydrogels

Single chemical or physical crosslinks

Weak & Brittle

Reinforced hydrogels

Double network



Gong, *Science* 2014, 344: 161

Nano-/micro-composite

Haraguchi, *Curr Opin Solid St M*, 2007,11: 47

Homogeneous network

Sakai, *Science* 2014, 343: 873

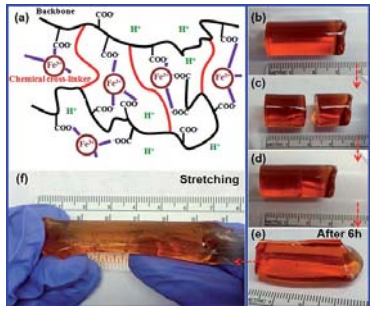
Dynamic crosslinks

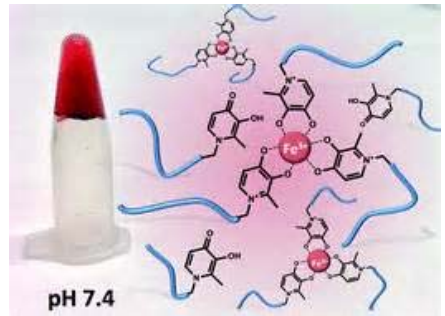
Gong, *Nat Mater* 2013, 12: 932

Dynamic crosslinks: reversible & healable

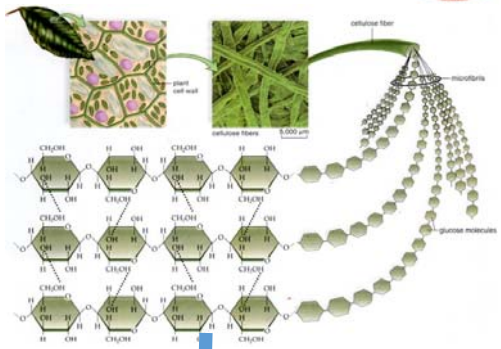
Chemical

- Disulfide bond
- Boronate ester bond
- Imine bond
- Diels-Alder reaction





Fe^{3+} coordination bond



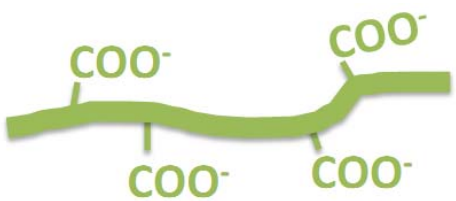
Carboxylation

Tempo-Cellulose Nanofiber (CNF)

Polyanionic cellulose (PAC)

Physical

- Metal coordination bond
- Hydrogen bond
- Host-guest interaction
- Hydrophobic interaction
- Electrostatic interaction



Monomer

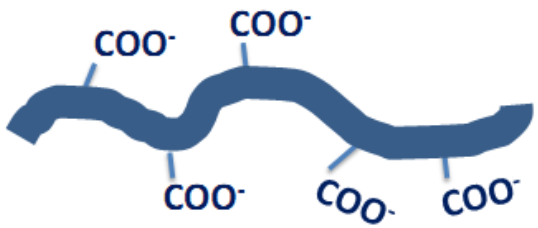
Polymerization

$FeCl_3$

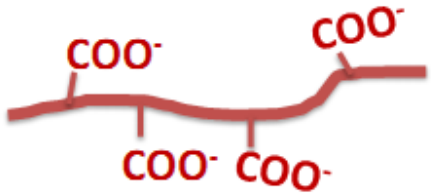
Composite hydrogels

Wang, *Polym Chem*, 2013, 4: 4601; Hawker, *Soft matter*, 2013, 43: 10314

Objective of this research



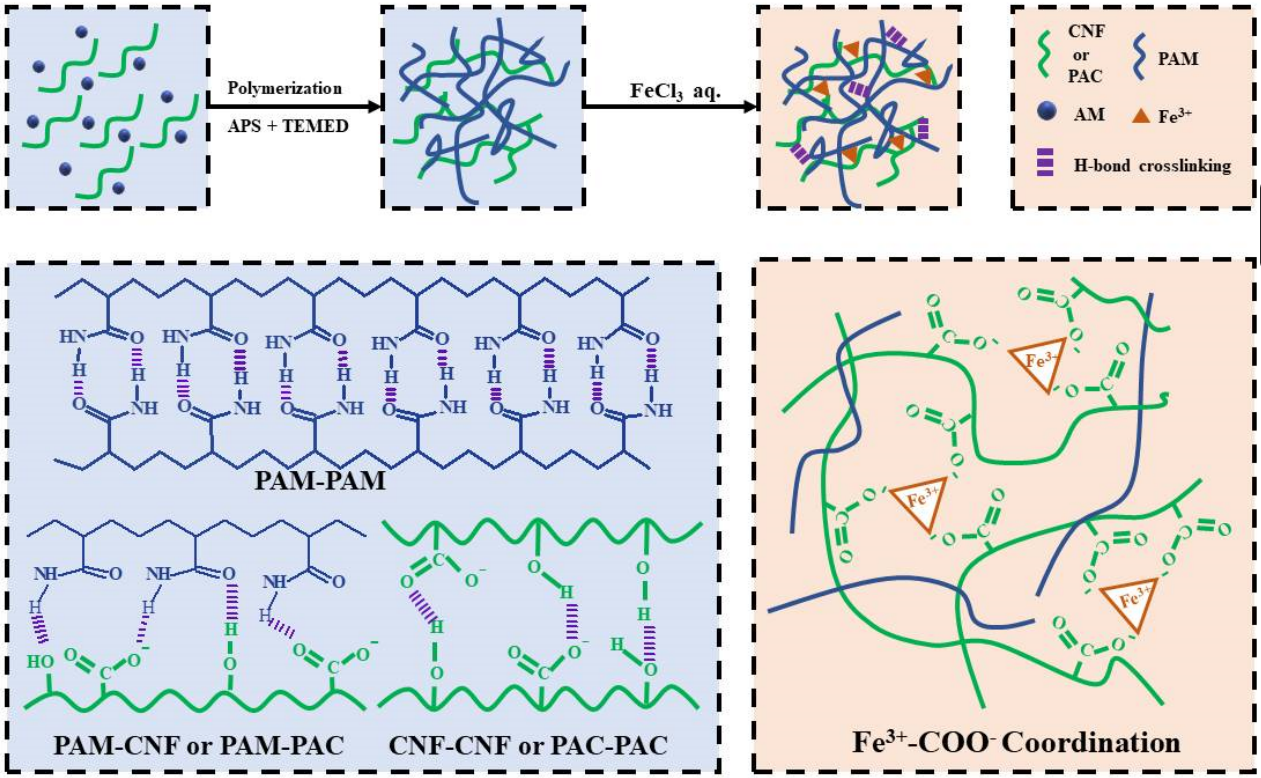
CNF: Nanofibers



PAC: Macromolecular chains

1. **To study the mechanical enhancement of carboxylated cellulose derivatives (CNF and PAC) and their coordinations with Fe^{3+} to PAM-based hydrogels.**
2. **To investigate the effect of structure characteristics of cellulose derivatives (nanofibers *vs* macromolecules) on mechanical properties.**
3. **To explore healing ability of PAM/CNF-Fe^{3+} and PAM/PAC-Fe^{3+} hydrogels.**

PAM/CNF-Fe^{3+} and PAM/PAC-Fe^{3+} composite hydrogels



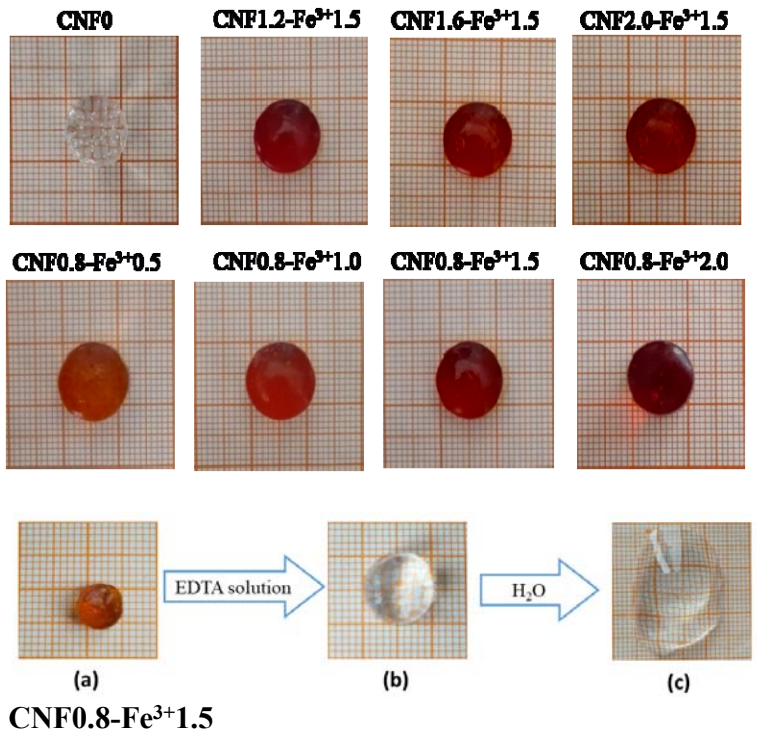
Two systems:

1. PAM/CNF-Fe^{3+} hydrogels

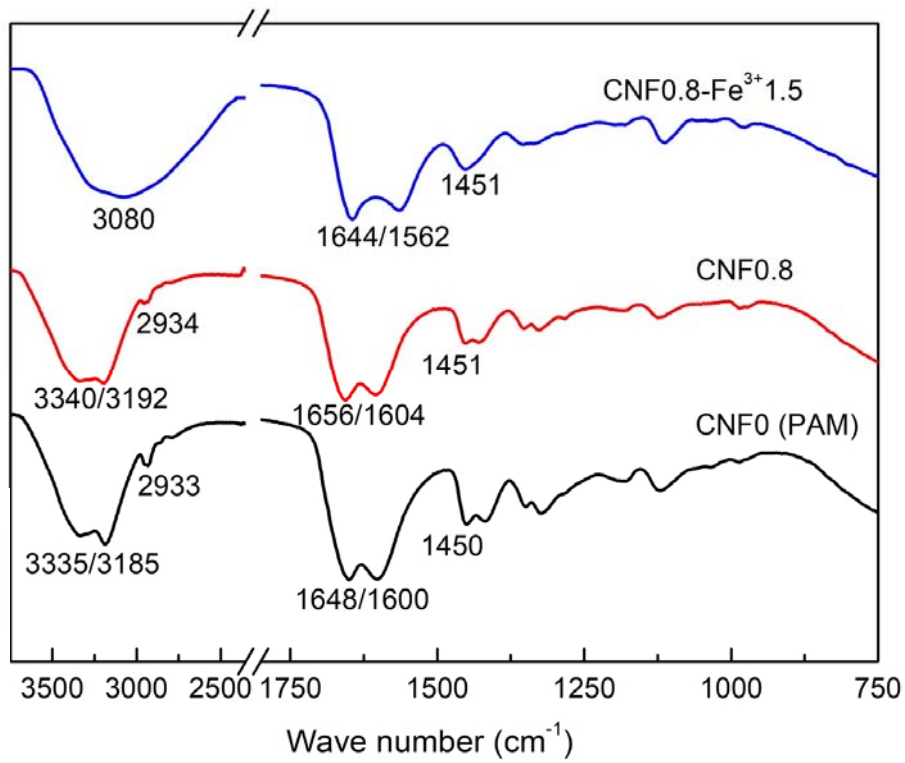
2. PAM/PAC-Fe^{3+} hydrogels

Inside gels, both H-bonding and Fe^{3+}-COO^- ionic coordination act as dual physical crosslinks.

PAM/CNF-Fe^{3+} composite hydrogels



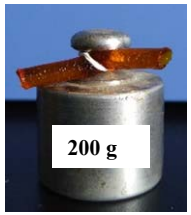
Fully physical hydrogels



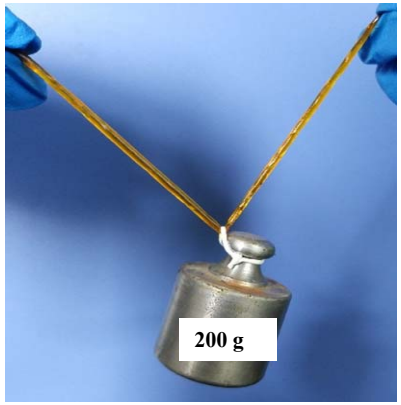
FTIR spectra

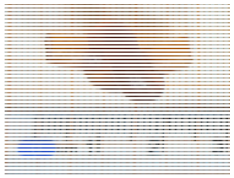
Characteristic peaks of $CONH_2$ groups on PAM shift with the introduction of CNF and/or Fe^{3+}, due to the alternation of H-bonding in gels.

Tensile properties for PAM/CNF-Fe^{3+} hydrogels

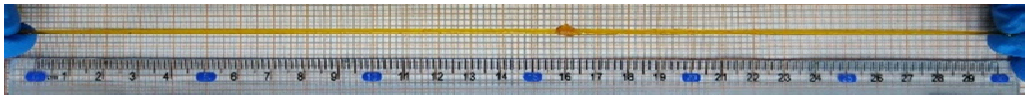


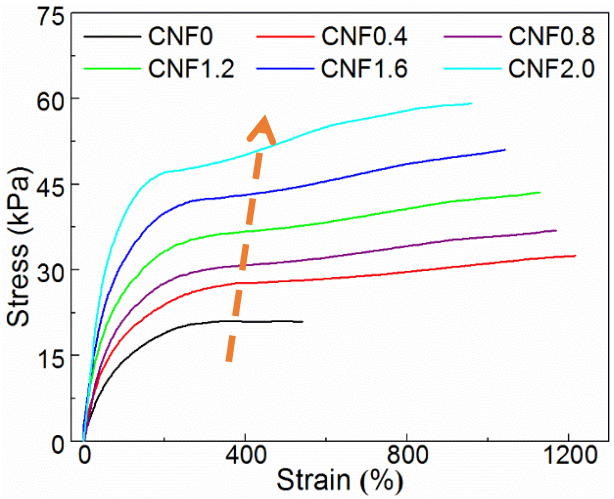
CNF2.0-Fe^{3+}1.5

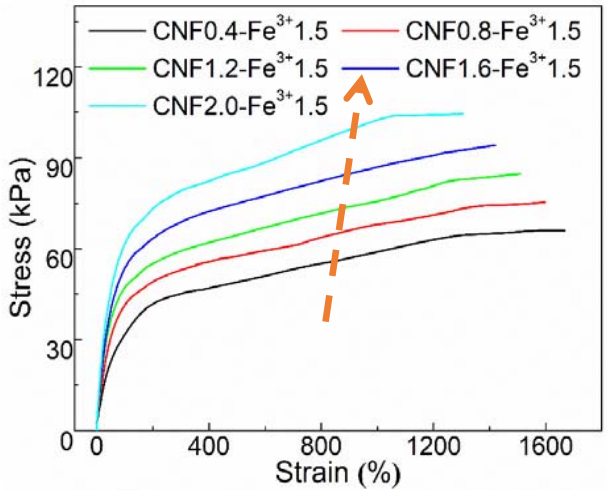


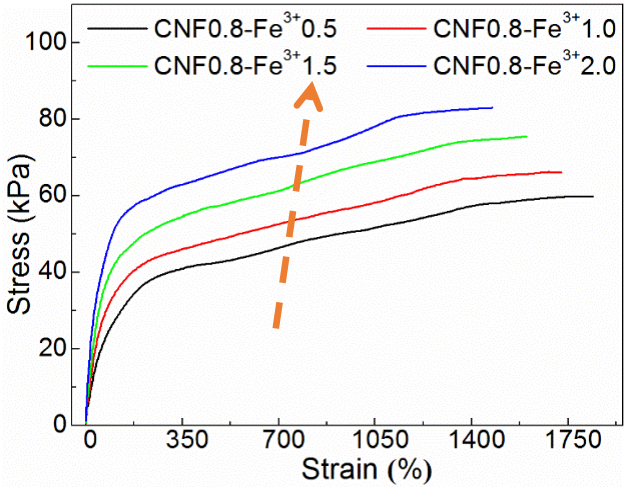


12X of extension



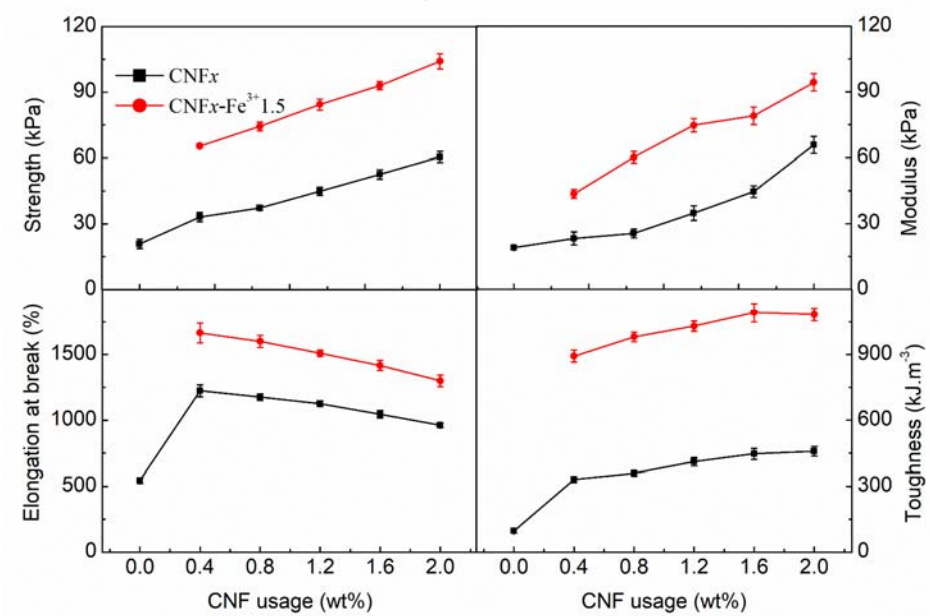




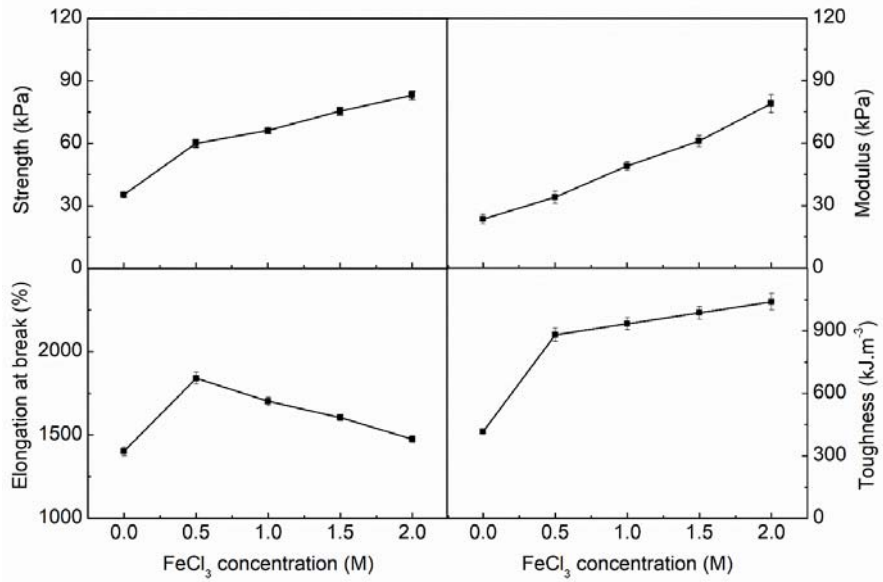


Tensile properties for PAM/CNF-Fe^{3+} hydrogels

CNF dosage dependence



Fe^{3+} concentration dependence



CNF increase, Strength, Modulus, and Toughness increase;
Elongation at break decrease, but higher than that of PAM gel.

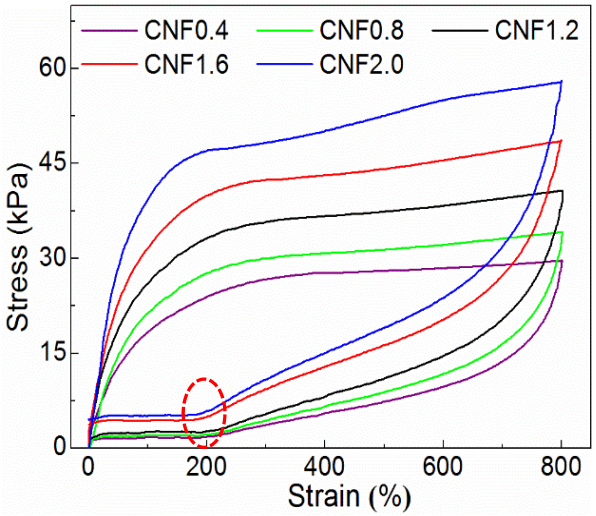
Fe^{3+} concentration increase, Strength, Modulus, and Toughness increase;
Elongation at break decrease, but higher than that of Fe^{3+}-free PAM/CNF gel.

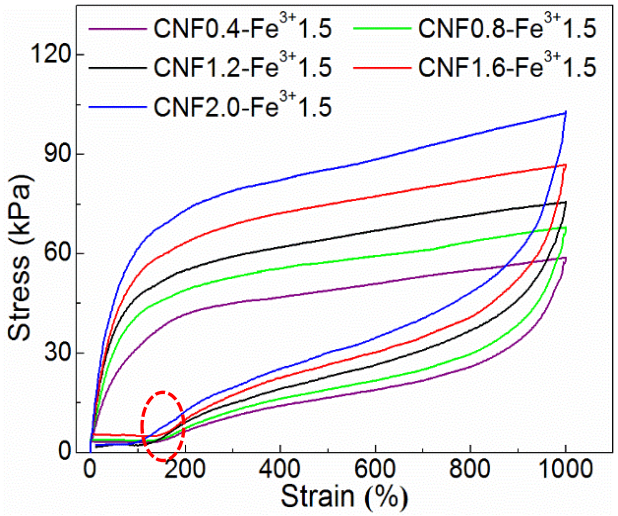
PAM-CNF H-bonding + **COO^{-}-Fe^{3+} ionic coordination**

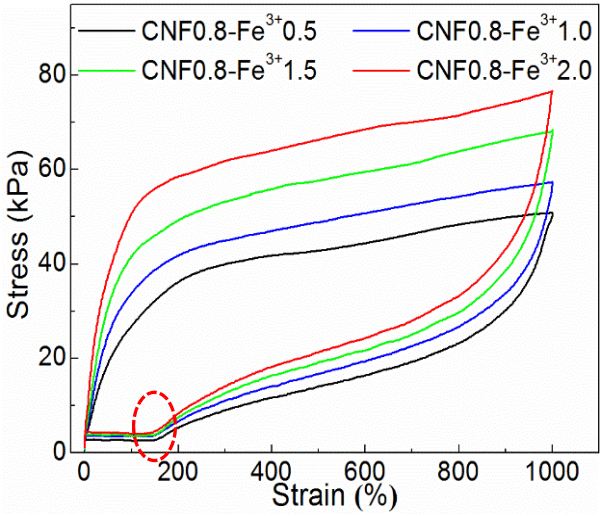
Single loading-unloading cycle

Cyclic tensile curves of hydrogels

Large hysteresis loops means energy dissipation mechanism

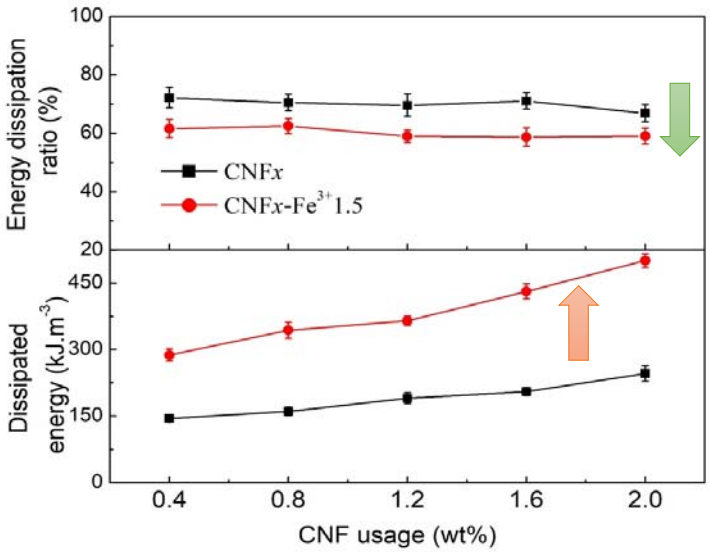


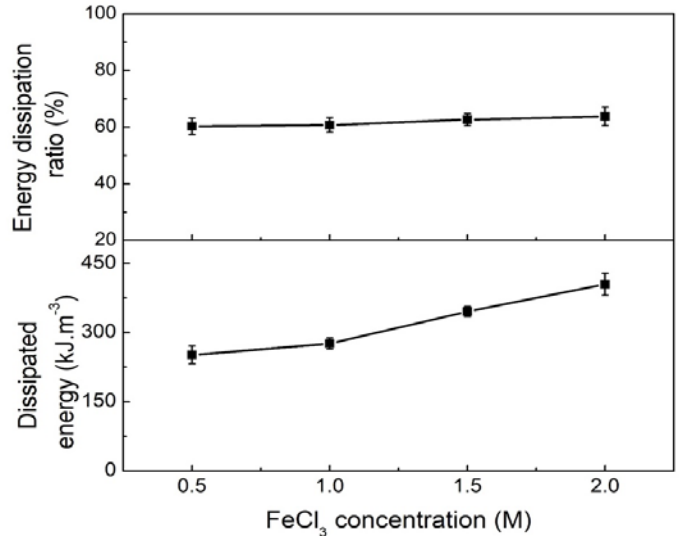




For PAM/CNF gels free of Fe^{3+}, the length recovered to around 200 % after the tensile unloading; the incorporation of Fe^{3+} improved self-recovery, reducing the recovery to below 150 % and even to 100 %.

Energy dissipation comparison of cyclic loading-unloading process



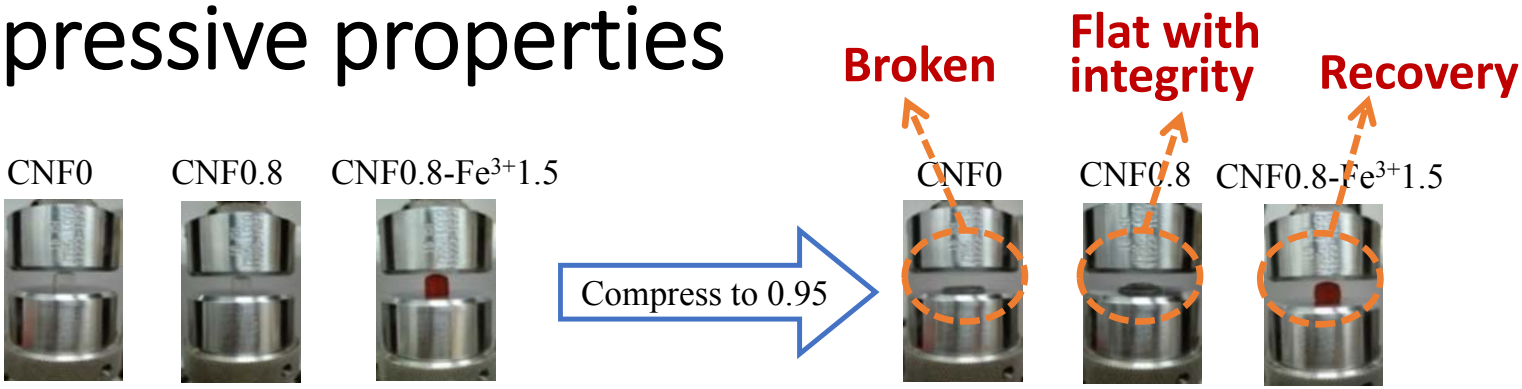


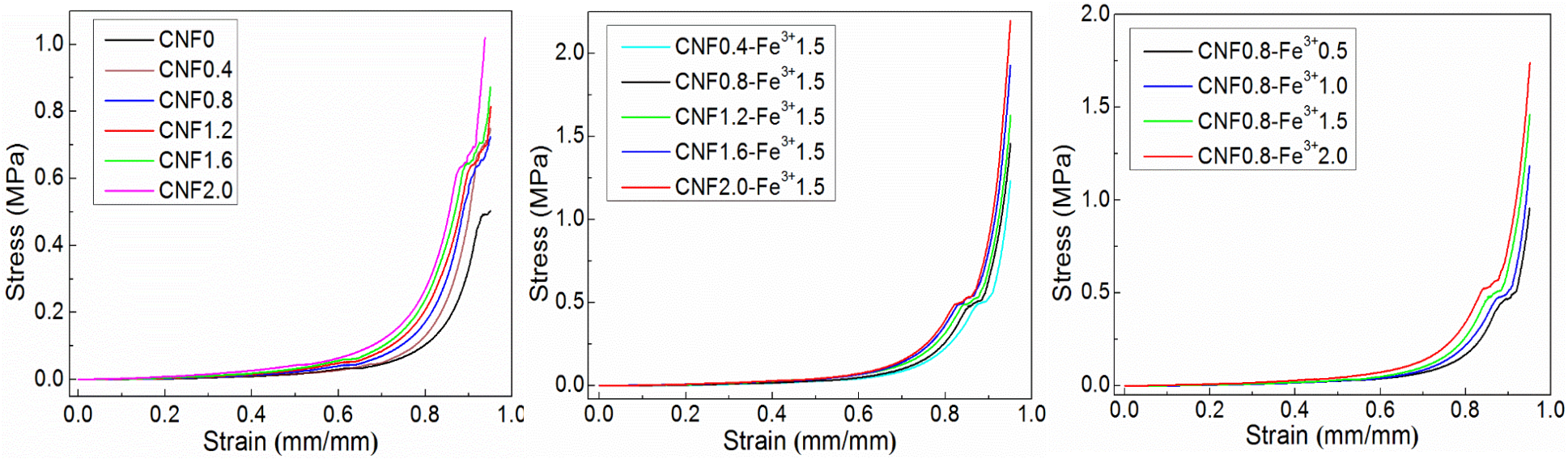
CNF or Fe^{3+} increase, dissipated energy increases

COO$^-$-Fe^{3+} bonds are more difficult to be broken than CNF-PAM HBs under exogenic actions, leading to the slight decrement of 10 % for energy dissipation ratio.

PAM-CNF H-bonding < COO$^-$-Fe^{3+} ionic coordination

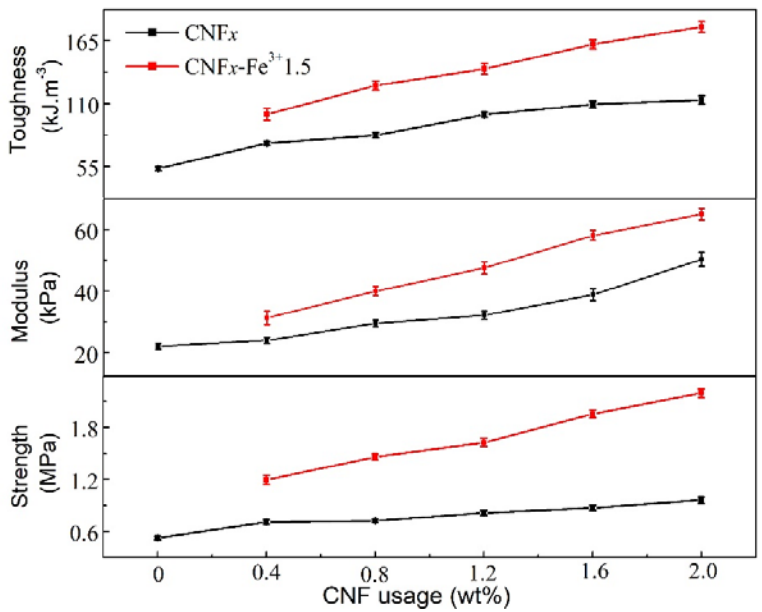
Compressive properties

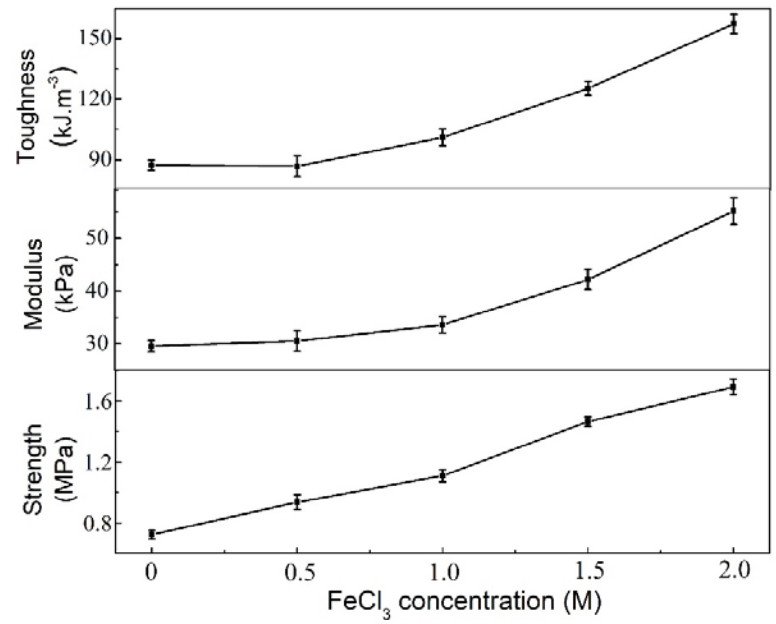




Compressive curves of hydrogels

Compressive properties



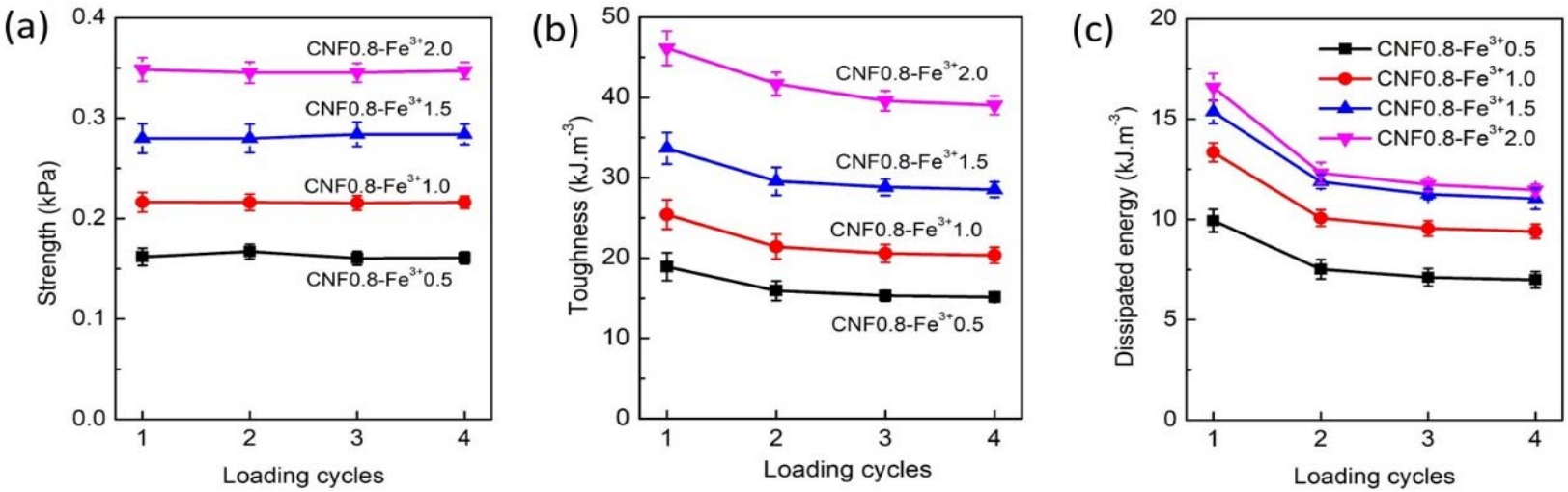


CNF increase, Strength, Modulus, and Toughness increase.

Fe^{3+} concentration increase, Strength, Modulus, and Toughness increase.

Four loading-unloading cycles

Strength, toughness and dissipated energy comparison

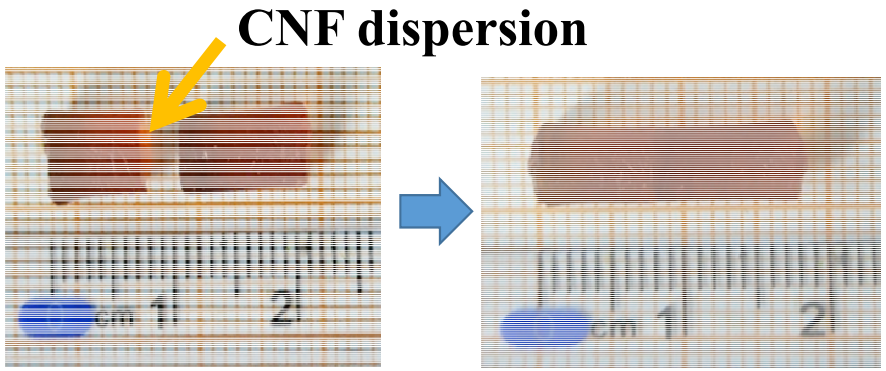


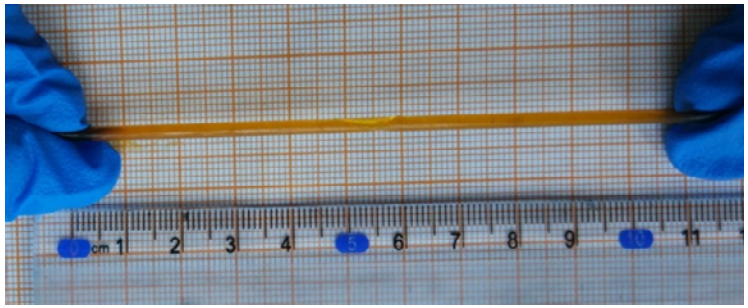
1. **The strength values are independent of cyclic numbers.**
2. **The toughness and dissipated energy show a slight decrease after the 1st cycle and then stabilized at a certain constant value in the following 3 ones.**

Some entanglements and/or H-bonding among PAM and CNF chains were destroyed under the 1st loading.

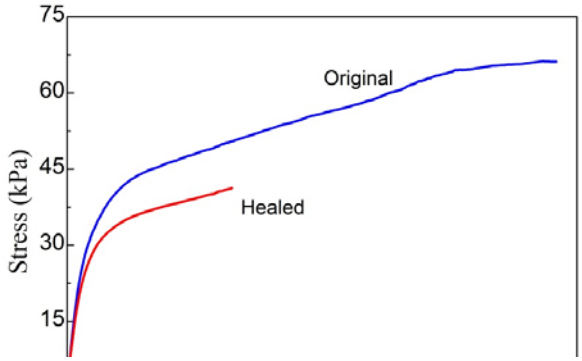
During the unloading process, Fe^{3+}-COO^{-} bonds reformed again, and PAM and CNF chains took more optimized and stable rearrangement.

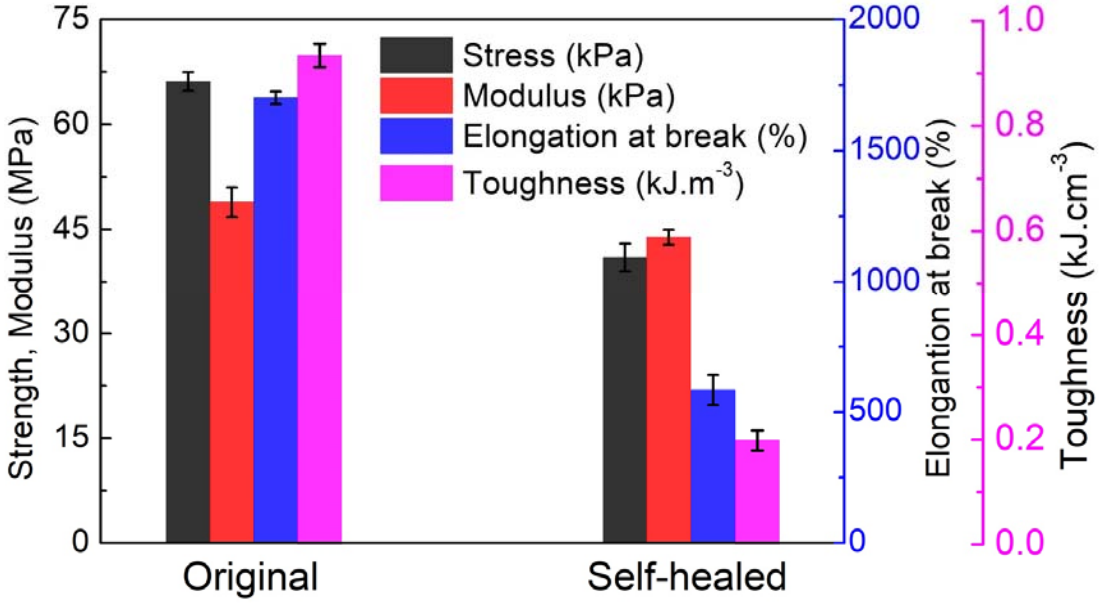
Healing ability





CNF0.8-Fe^{3+}1.0 Gel





CNF dispersion assisted healing

A summary for PAM/CNF-Fe^{3+} composite hydrogels

PAM/CNF-Fe^{3+} nanocomposite hydrogels

CNF-PAM H-bonding

+

COO^{-}-Fe^{3+} ionic coordination

Dual physical crosslinks

Excellent & adjustable mechanical properties

Healing ability

PAM/PAC-Fe^{3+} composite hydrogels

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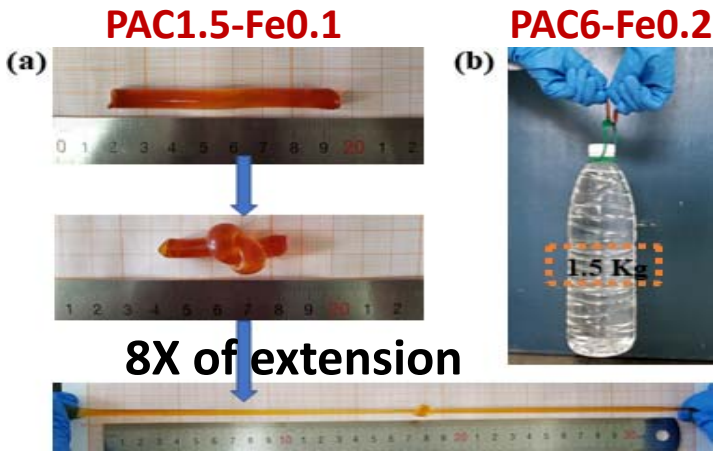
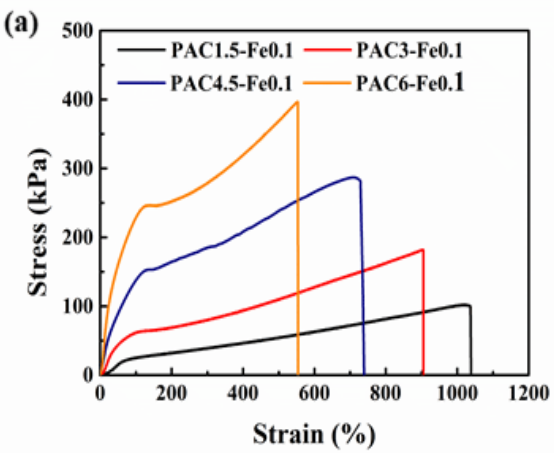
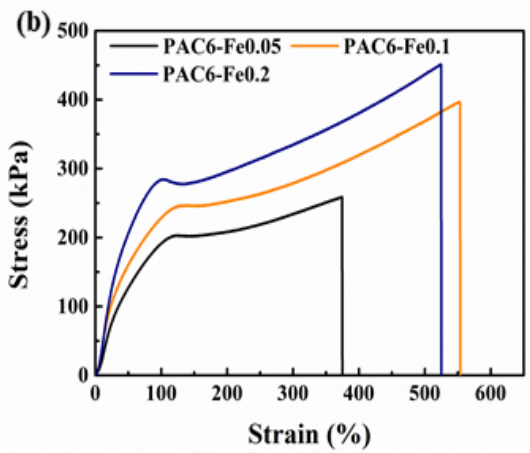
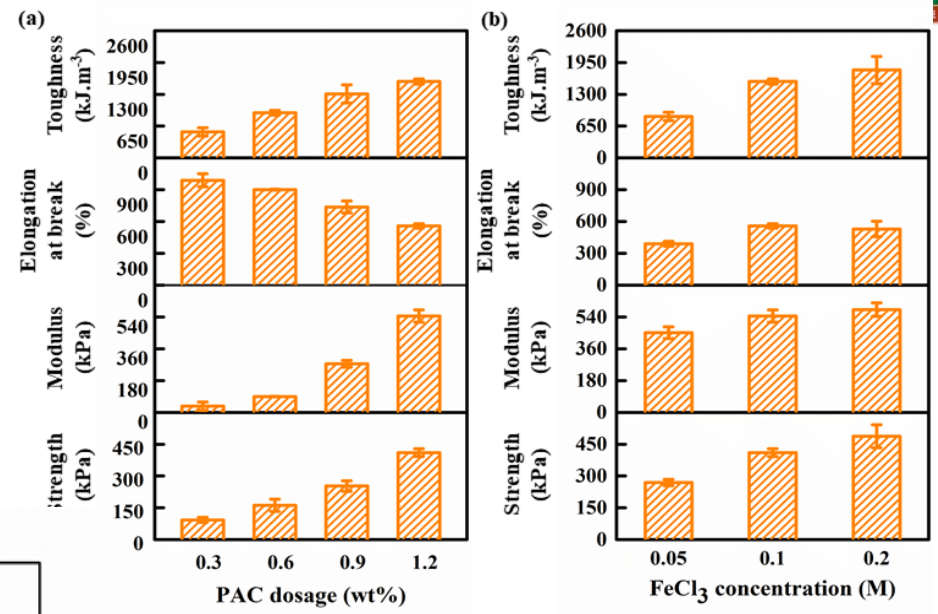
Tensile properties of PAM/PAC-Fe^{3+} composite hydrogels





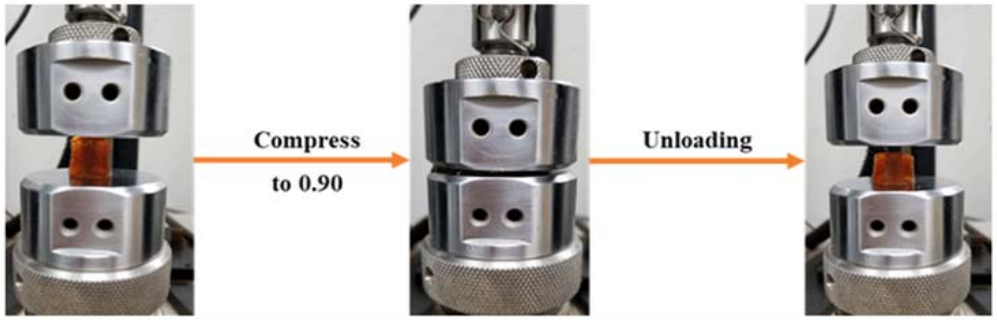


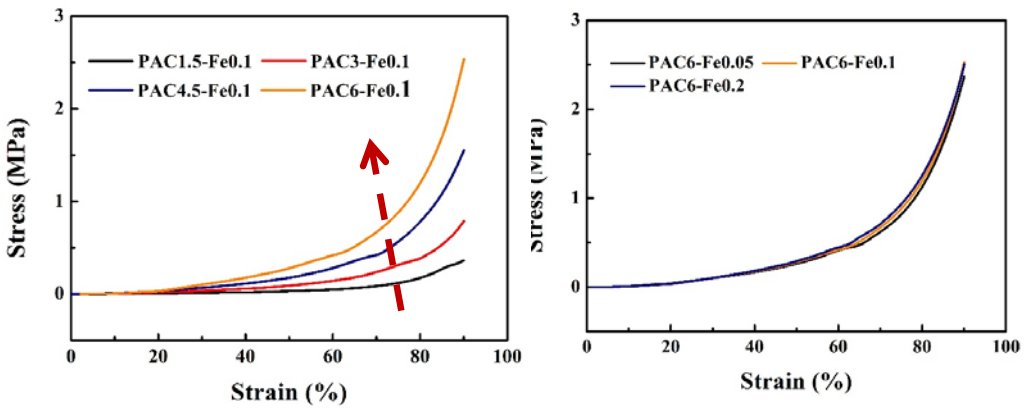


- PAC increase, Strength, Modulus, and Toughness increase; Elongation at break decrease.
- Fe^{3+} concentration increase, Strength, Modulus, Toughness and Elongation at break increase slightly.

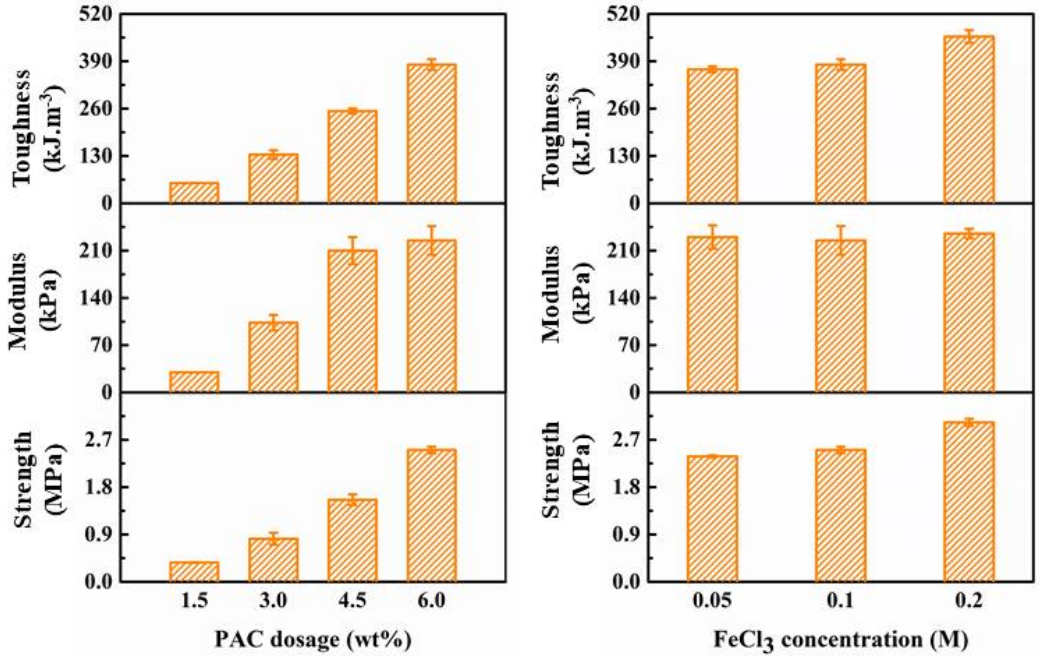
Compressive properties of PAM/PAC-Fe^{3+} composite hydrogels

PAC6-Fe0.1





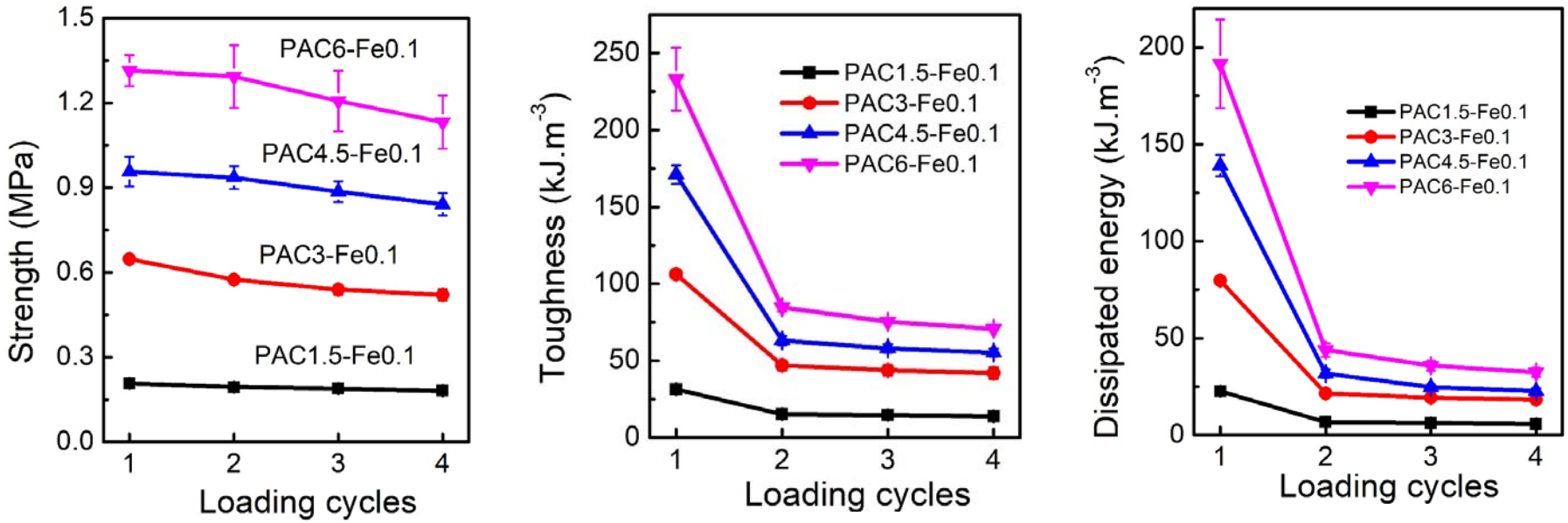
Compressive curves



1. **PAC increase, Strength, Modulus, and Toughness increase.**
2. **Fe^{3+} concentration increase, Strength and Toughness increase very slightly; Modulus doesn't change almost.**

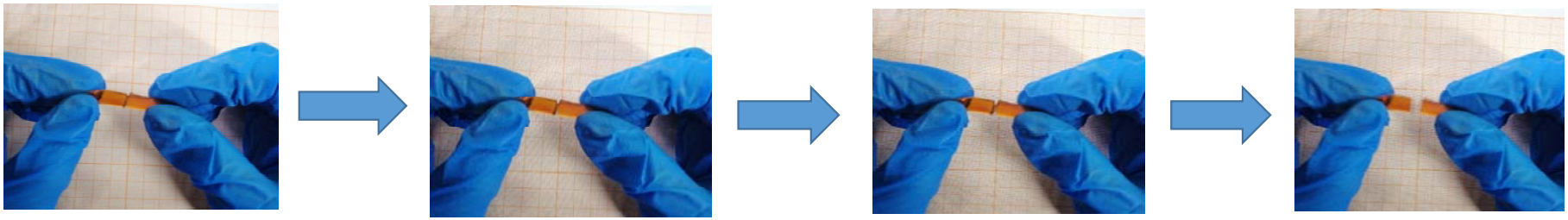
Four loading-unloading cycles

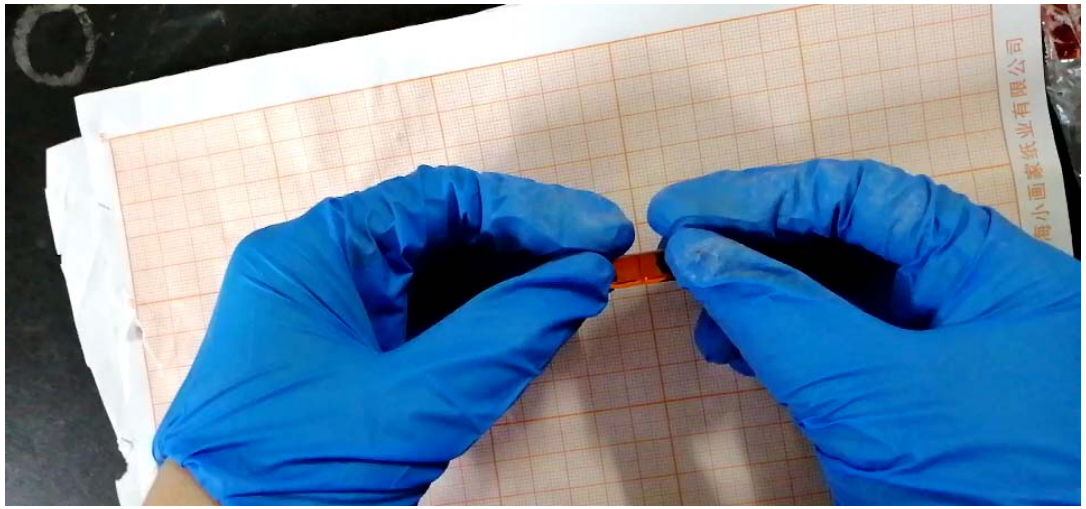
Strength, toughness and dissipated energy comparison



1. **The strength values gradually decreased with cyclic numbers.**
2. **The toughness and dissipated energy show a great decrease after the 1st cycle and then stabilized at a certain constant level in the following 3 ones.**
3. **The cyclic compression behavior of PAC-Fe systems is different from those of CNF-Fe ones.**

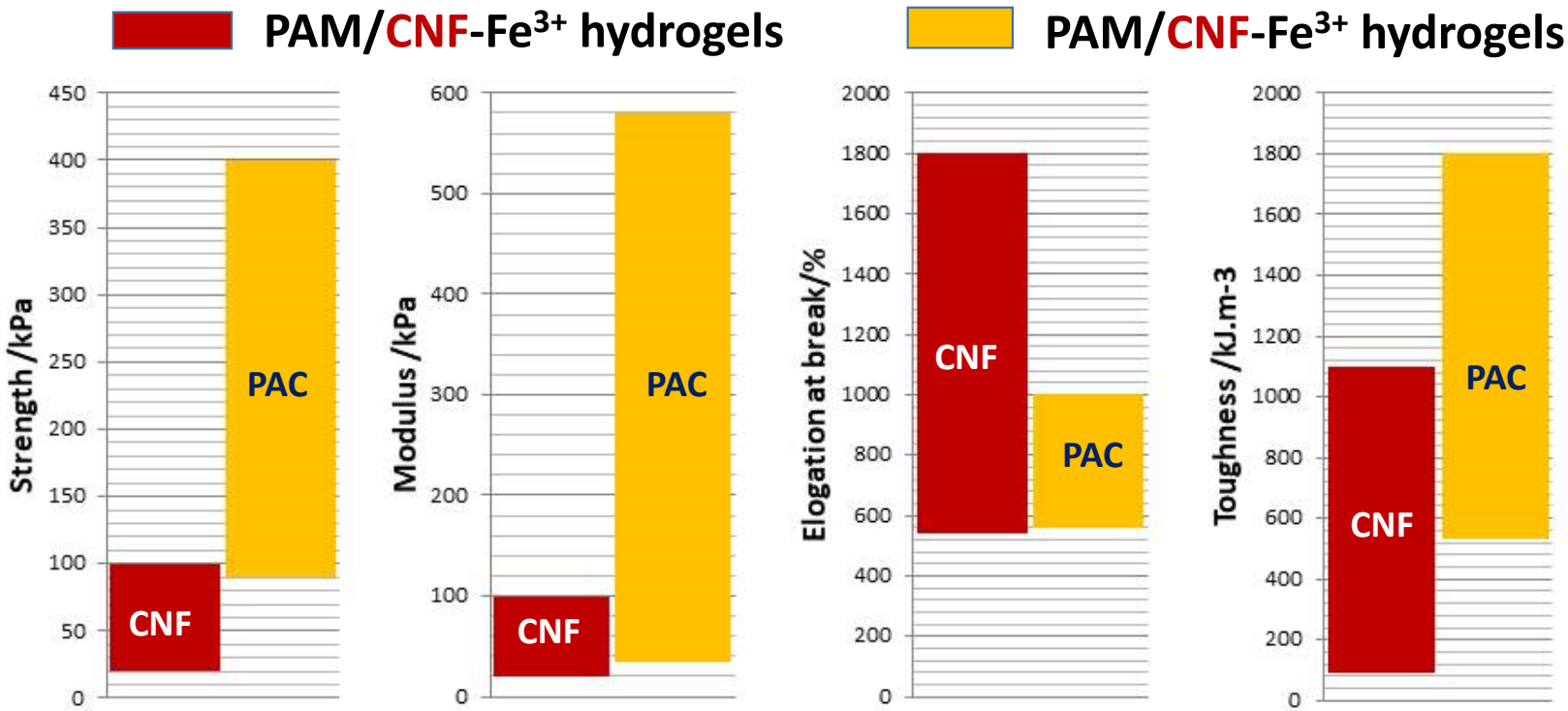
Healing ability





Unlike PAM/CNF-Fe^{3+} systems, PAM/PAC-Fe^{3+} ones cannot heal, even if under the assistance of CNF dispersion, PAC solution or Fe^{3+} solution.

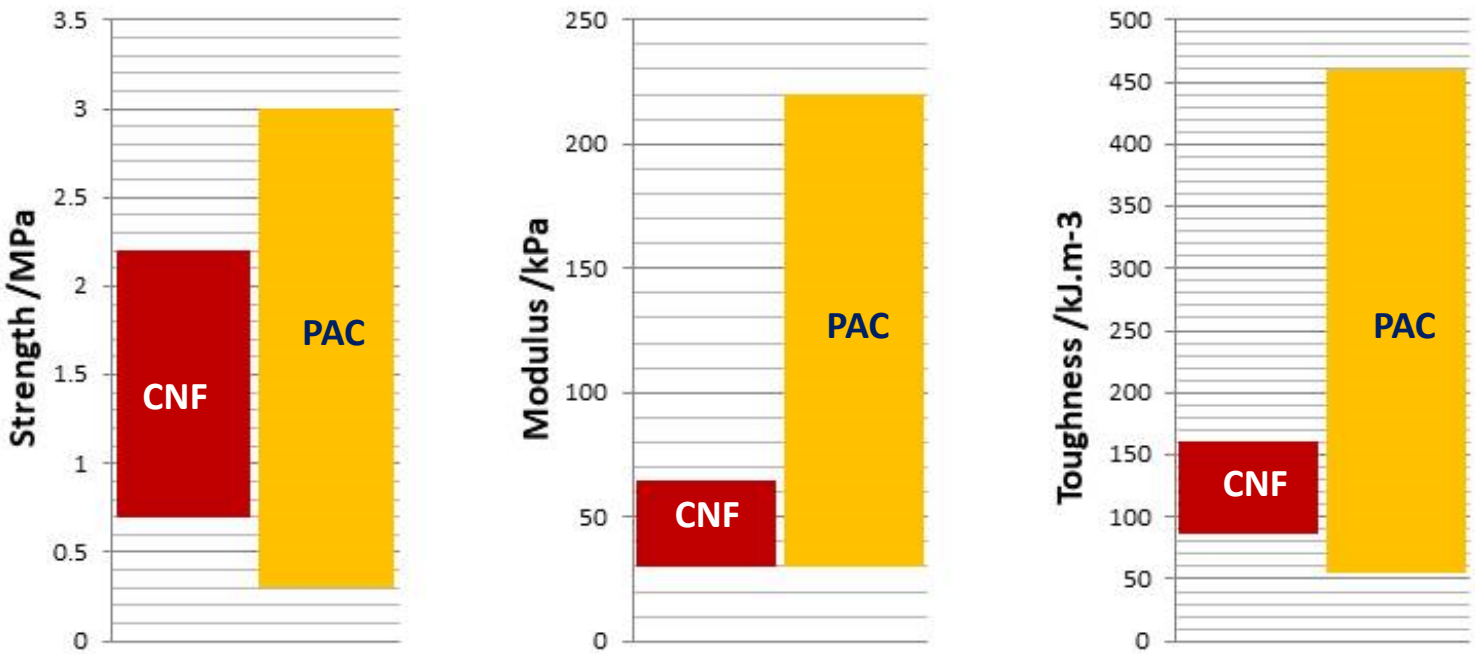
Comparison for tensile properties



1. For tensile strength and modulus, PAC-based hydrogels have broader ranges and higher values than those of CNF-based ones.
2. For elongation at breaks, PAC-based hydrogels have more narrow range than CNF-based ones.
3. For toughness, higher values for PAC systems can be obtained.

Comparison for compressive properties

PAM/CNF-Fe^{3+} hydrogels PAM/CNF-Fe^{3+} hydrogels



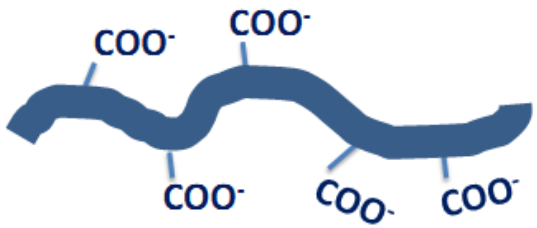
1. For compressive strength and modulus, PAC-based hydrogels have broader ranges or higher values than those of CNF-based ones.
2. For toughness, PAC-based hydrogels have broader and higher values than those of CNF-based ones.

Broader ranges or higher values for PAC-based systems than those of CNF-based ones

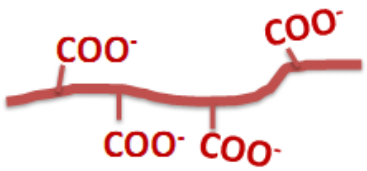
Higher –COO^- content in PAC than in CNF; Higher dosage for PAC than CNF in composite gels

More COO^--Fe^{3+} bonds in PAC systems

CNF

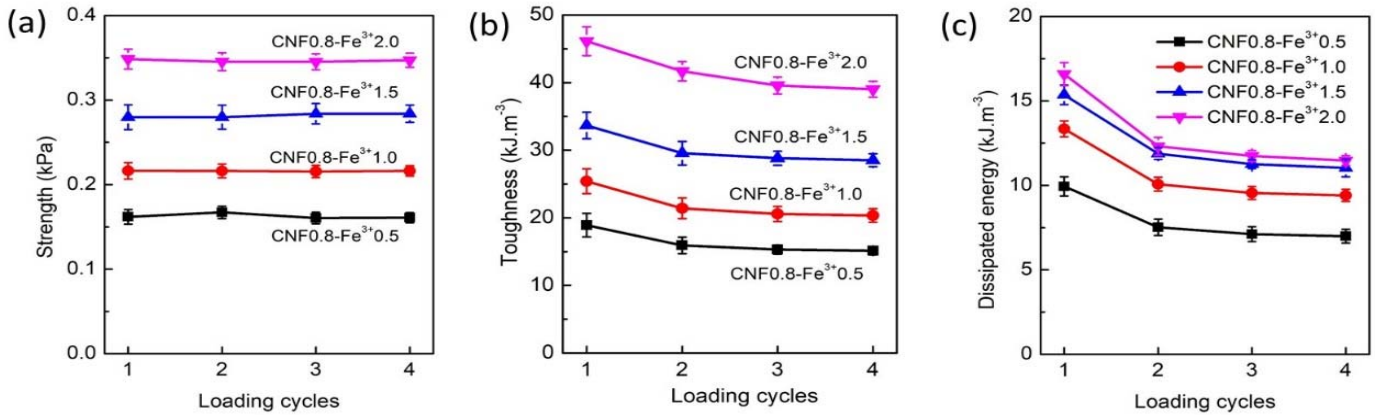


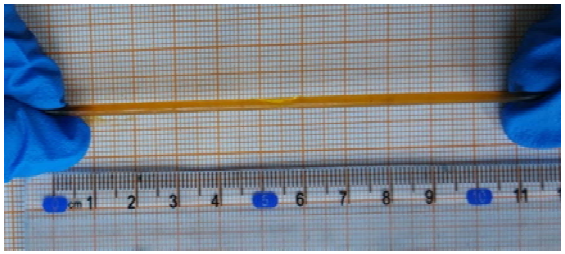
PAC



COO^-: 1.56 mmol/g	×2.5	COO^-: 3.87 mmol/g
m_{max}: 2 wt% of AM	×3	m_{max}: 6 wt% of AM

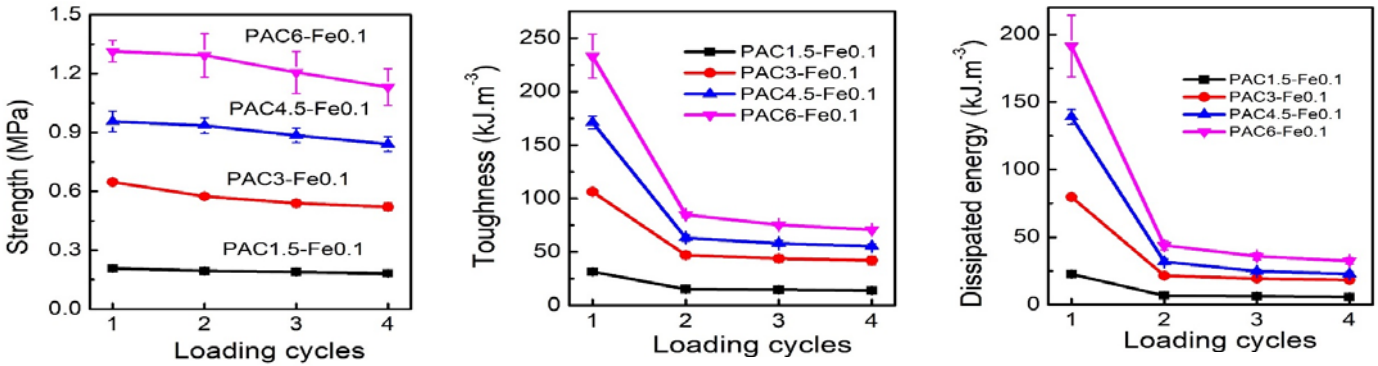
Comparison for Cyclic compression and healability

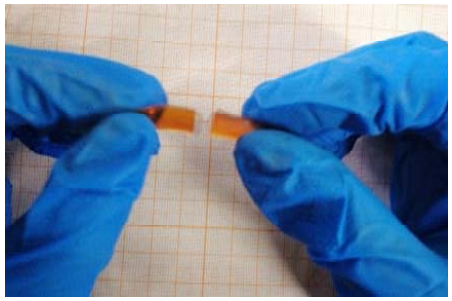




Healable

CNF system vs PAC system





Unhealable

Anti-fatigue: CNF-gels > PAC-gels

Healability: CNF-gels √ PAC-gels x

Conclusions

1. H-bonding between PAM and CNF or PAC, as well as COO^--Fe^{3+} ionic coordination serve as dual physical crosslinks in PAM/CNF-Fe^{3+} and PAM/PAC-Fe^{3+} composite hydrogels;
2. Both PAM/CNF-Fe^{3+} and PAM/PAC-Fe^{3+} composite hydrogels reveal excellent mechanical performances which are modulatable through changing CNF or PAC dosage and/or Fe^{3+} concentration;
3. For strength, modulus and toughness, PAC-based hydrogels show broader adjustable ranges and higher values than CNF-based ones;
4. PAM/CNF-Fe^{3+} hydrogels are more anti-fatigued than PAM/PAC-Fe^{3+} ones, and the former are capable of healing, while the latter cannot.

Thanks for your attention

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