Tailoring Interfacial Layer Structures for Nanocellulose/Polymer Composites

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TAPPI

Contents

- General introduction
- Preparation of PEG-TOCN/CTA composites
- Interfacial layer thickness vs. material properties
- Grafting density vs. material properties
- Conclusion

Contents

General introduction

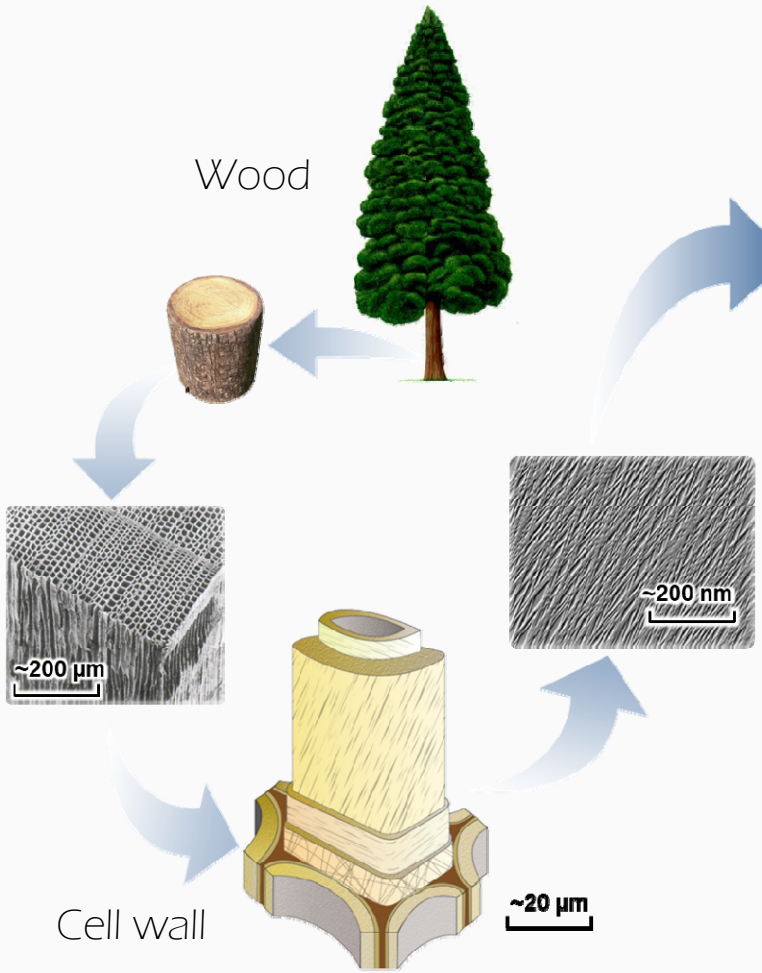
Preparation of PEG-TOCN/CTA composites

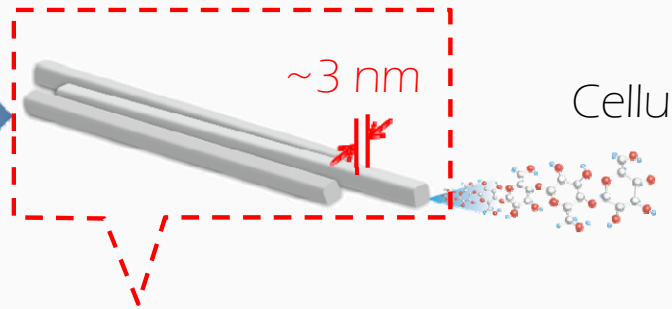
Interfacial layer thickness vs. material properties

Grafting density vs. material properties

Conclusion

Hierarchical structure of native cellulose



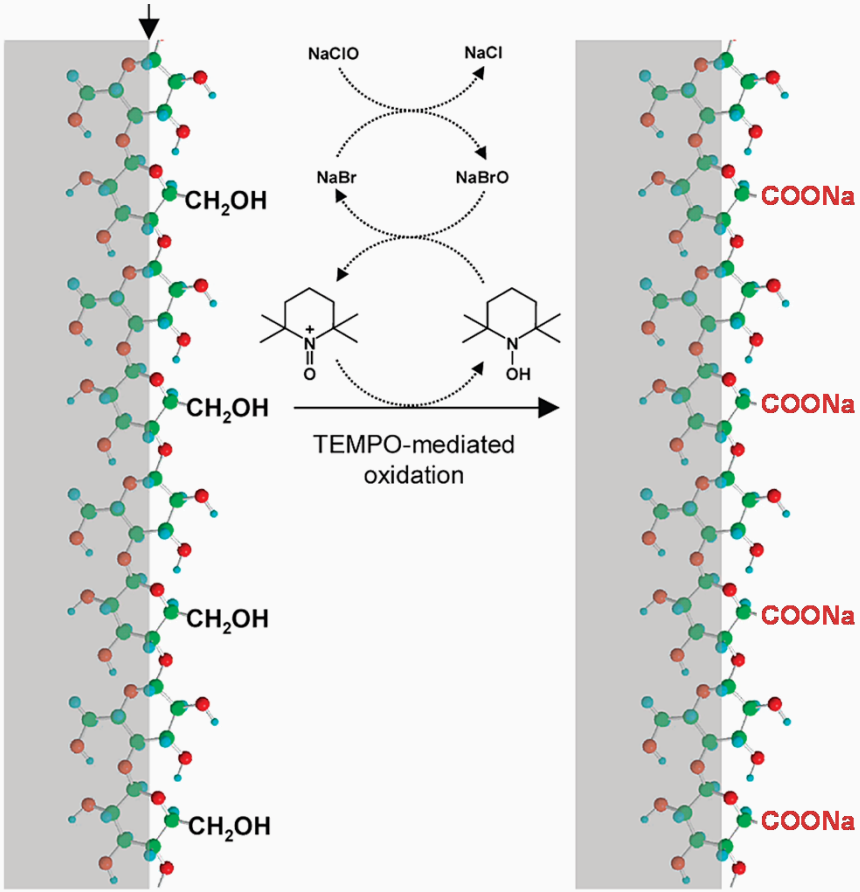


Cellulose microfibril

- High aspect ratio
- High crystallinity
- High elastic modulus (130–150 GPa)
- High tensile strength (3 GPa)
- Low coefficient of thermal expansion (6 ppm K^{-1})

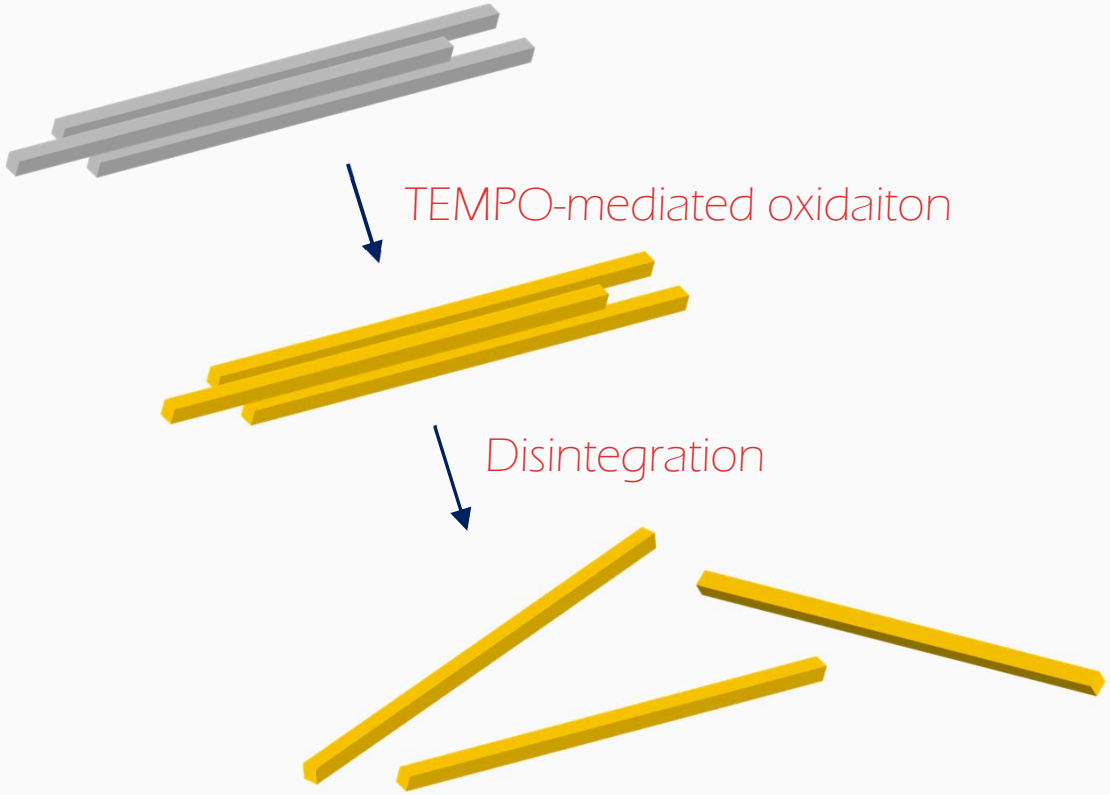
TEMPO-mediated oxidation

Fibril surface



Okita et al. 2010

Cellulosic material
(Bundles of cellulose microfibril)

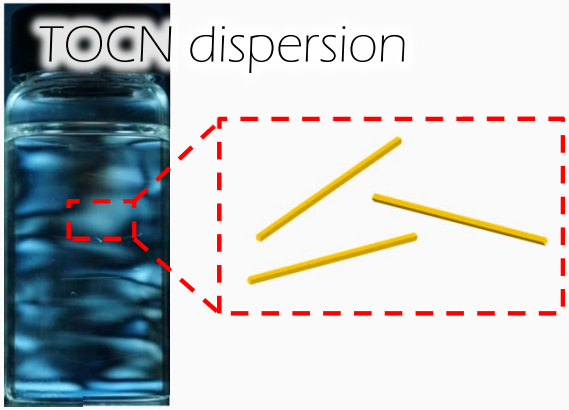


TEMPO-oxidized cellulose nanofibrils (TOCN)

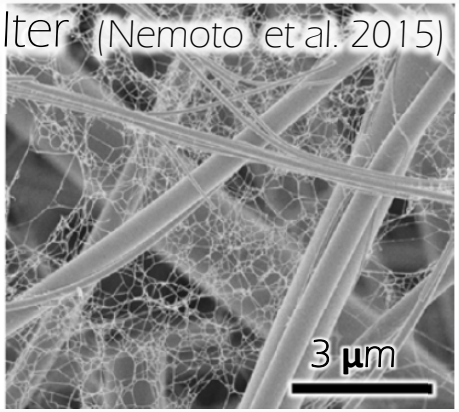
Application of TOCN

Barrier film (Fukuzumi et al. 2009)

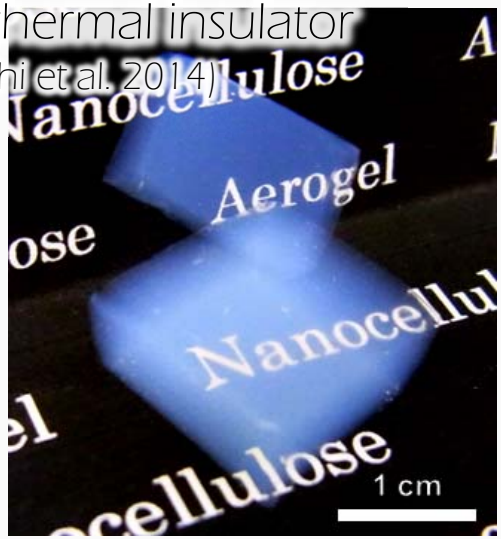
TOCN dispersion



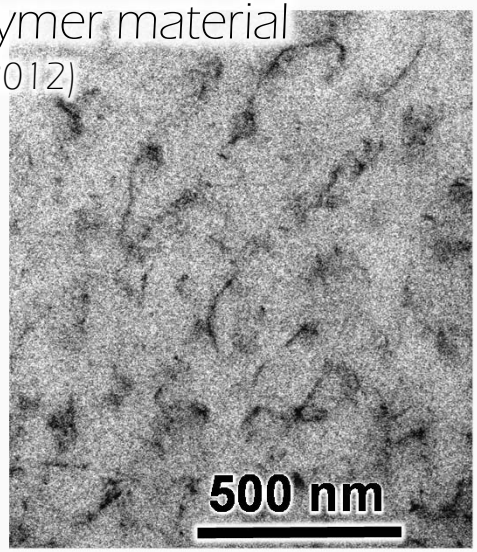
Air filter (Nemoto et al. 2015)



Transparent thermal insulator (Kobayashi et al. 2014)



Reinforcement for polymer material (Fujisawa et al. 2012)



Nanocellulose as reinforcement filler

Advantages of nanocellulose

Large interfacial area between nanocellulose and polymer matrix

↳ effective reinforcement is achieved

↳ interfacial properties occupy the bulk properties

✓ Good dispersibility of nanocellulose

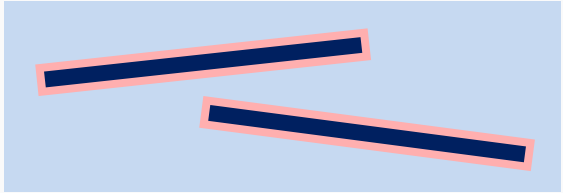
✓ Good interaction between nanocellulose/polymer

Surface modification of nanocellulose

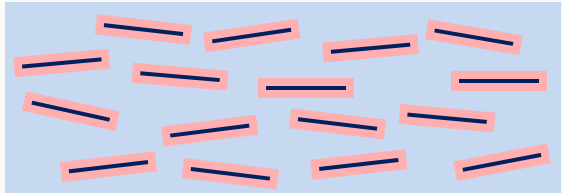
- Functionalization: acetylation, silylation etc.
- Introduction of polymer chains: grafting, absorption

↳ Dispersibility and crystallinity of nanocellulose is affected by the modification

Micron-sized filler



Nano-sized filler



Polymer matrix

Filler

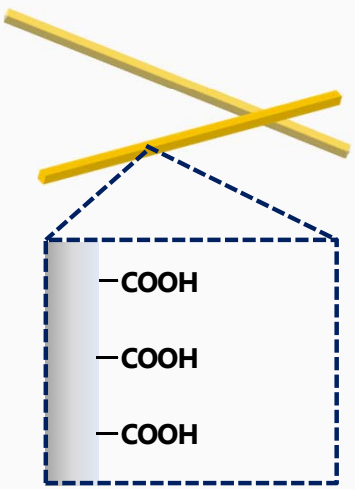
Interfacial layer

Objective of the present study

To investigate the relationship between the interfacial structure and material properties of nanocellulose/polymer composites

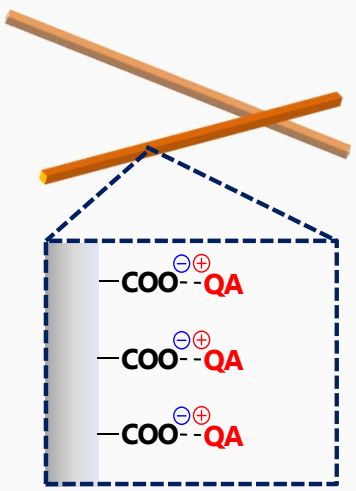
Surface modification with maintaining dispersibility and crystallinity

TOCN



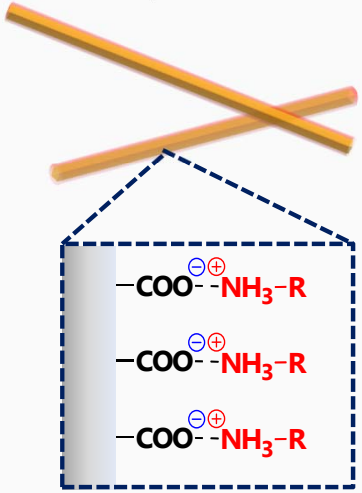
Okita et al. 2011

TOCN-QA



Shimizu et al. 2014

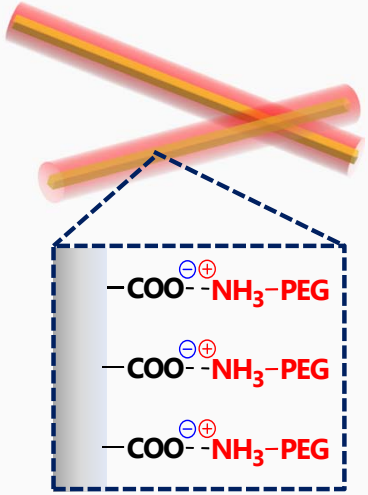
TOCN-aliphatic amine



R = $C_{2n}H_{4n+1}$ (n = 5 ~ 8)

Fujisawa et al. 2012

PEG-TOCN



Fujisawa et al. 2013

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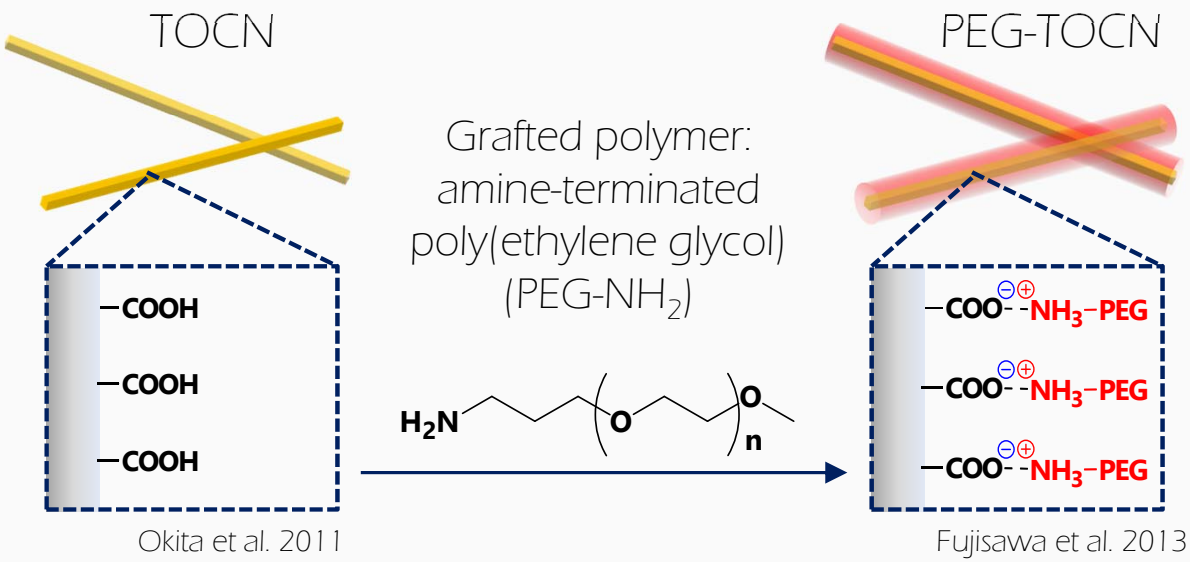


Okita et al. 2011

Fujisawa et al. 2013

POINT 1 TOCNs can be individually dispersed with/without modification

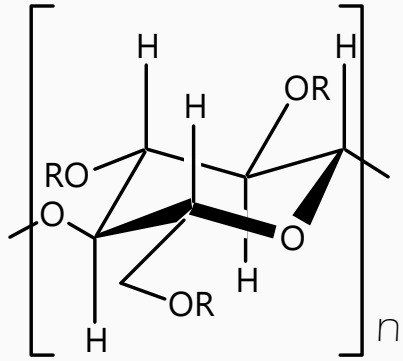
POINT 2 Grafted-chain length and grafting ratio can be controlled

Objective of the present study

■ Polymer matrix : to investigate the effects of the interfacial structure only

Cellulose triacetate (CTA)

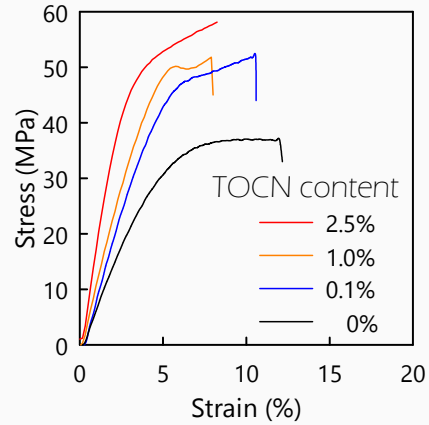
R = CH_3CO or H
DS ≈ 2.9



CTA
- has low crystallinity*
- dissolves in TOCN dispertant
- interacts with TOCNs**
- interacts with PEG***

- Improvement in material properties is required as optical films and osmosis membranes

TOCN/CTA composites (pre-experiment)



*Sata et al. 2004, Fan et al. 2009, **Kong et al. 2014, ***Gutierrez et al. 2017.

Objective of the present study

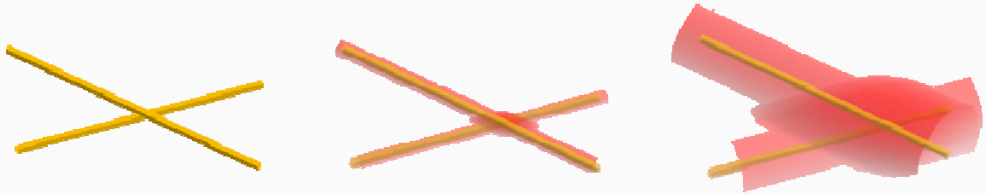
Factors affecting the material properties of TOCN/CTA composites

Dispersibility — TOCN and PEG-TOCN have good dispersibility

Interfacial interaction — the same matrix, filler, and grafted polymer

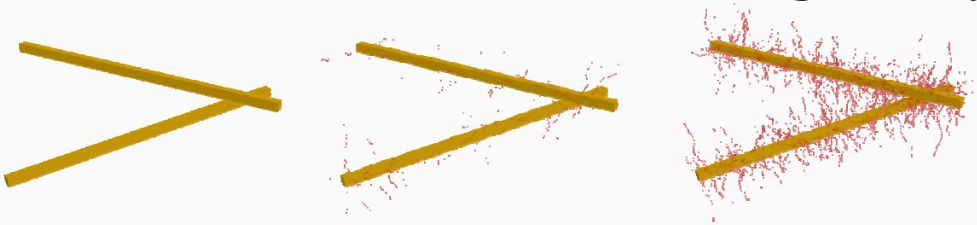
Interfacial layer thickness

No modification → Thick grafted layer



Grafting density

No modification → Dense grafted layer



Contents

General introduction

Preparation of PEG-TOCN/CTA composites

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Grafting density vs. material properties

Conclusion

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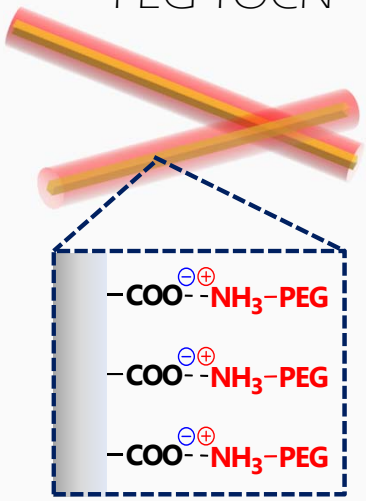
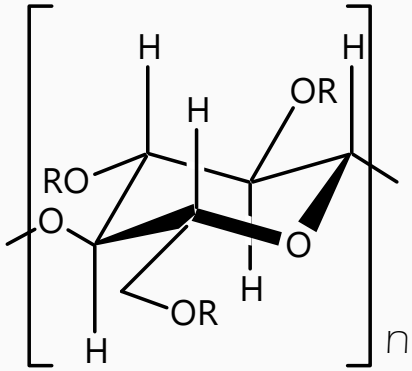
PEG-TOCN



(PEG M_w = 1000)

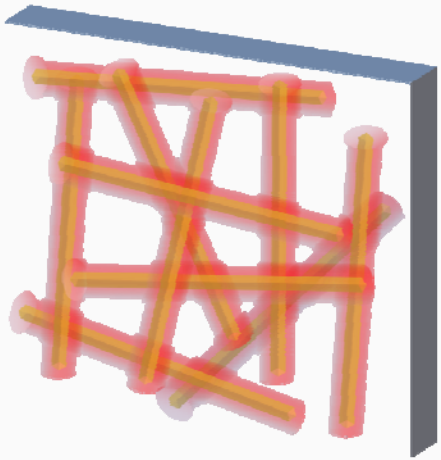
+

Cellulose triacetate (CTA)



→

PEG-TOCN/CTA composite film



Objective; to observe the reinforcing effect of PEG-TOCN

Preparation of PEG-TOCN/CTA composites

Softwood bleached kraft pulp

▼ TEMPO-oxidation

TEMPO-oxidized pulp

▼ Suspending in water

▼ Ultrasonication (disintegration)

TOCN/water dispersion

▼ Gelation with HCl, washing

▼ Exchanging solvent (water → ethanol → chloroform)

▼ Grafting PEG-NH_2 (M_w = 1000)

▼ Ultrasonication (disintegration)

PEG-TOCN/chloroform dispersion

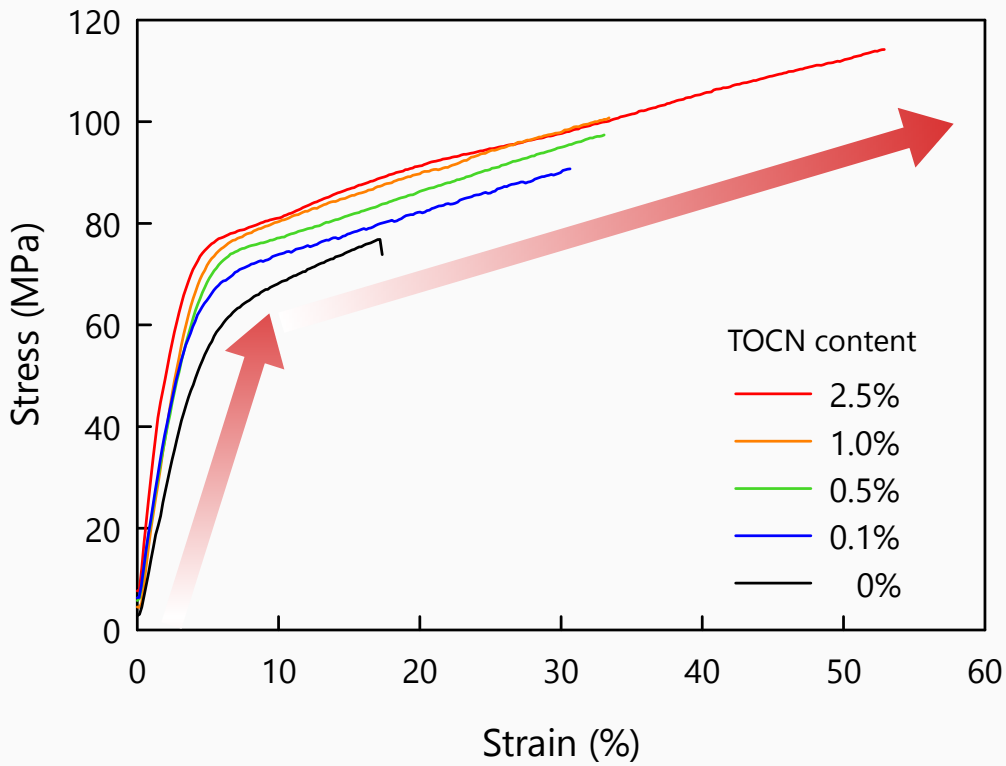
▼ Mixing with CTA solution

▼ Cast-drying (23°C, 1 atom, 1 day)

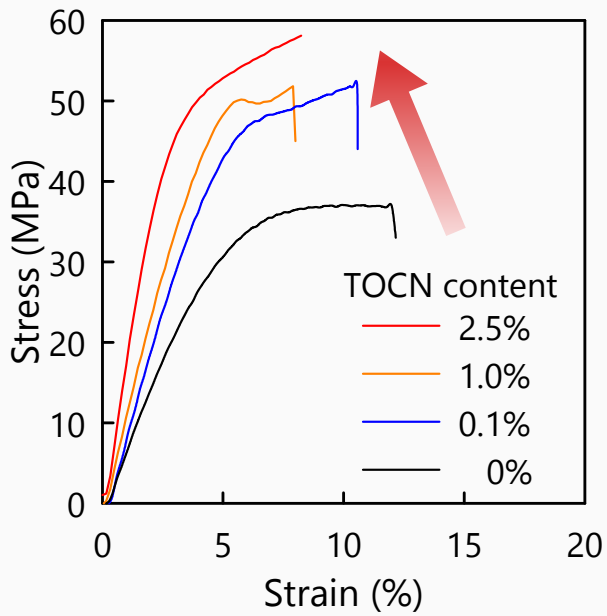
PEG-TOCN/CTA composite film

Mechanical properties of composites

PEG-TOCN/CTA composite films

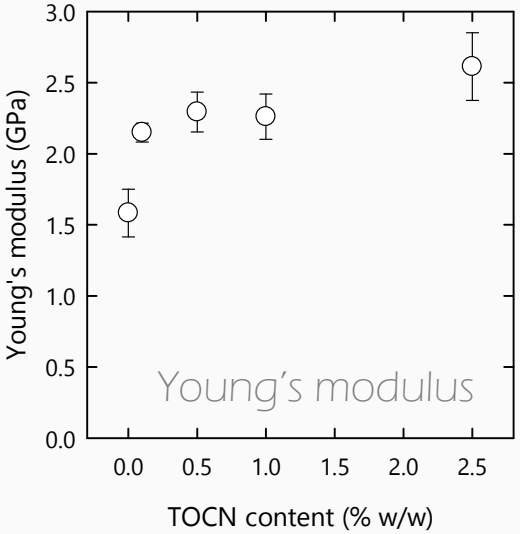


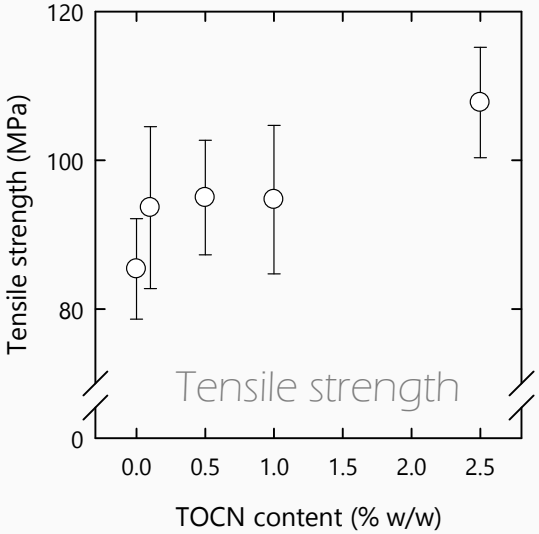
TOCN/CTA composite films
(pre-experiment)

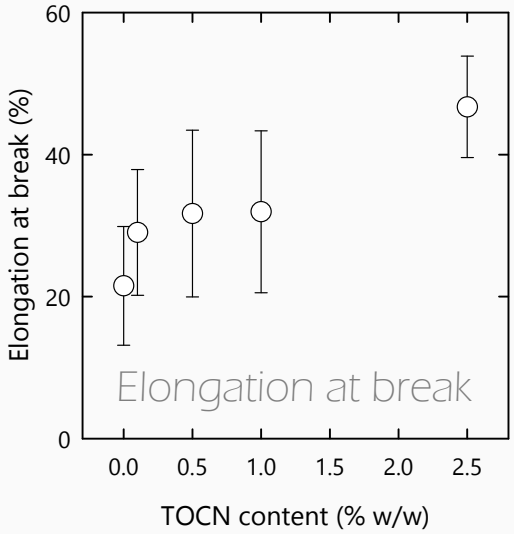


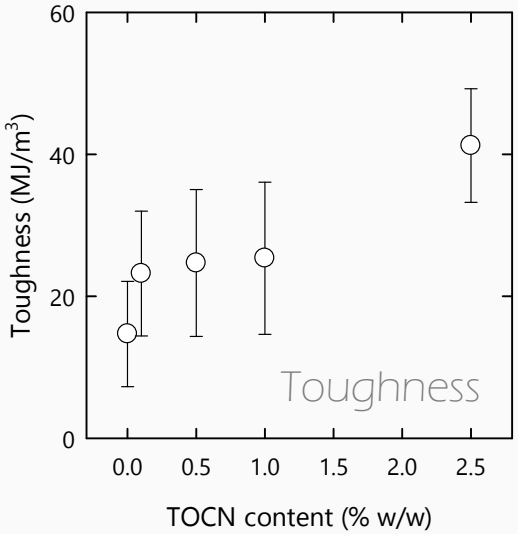
Stiff, strong, ductile, and tough!

Mechanical properties of composites









- Increase in Young's modulus
  ↳ good interaction between PEG-TOCN and CTA matrix
- Increase in elongation at break
  ↳ interfacial PEG layer supported the deformation of CTA

- Young's modulus, tensile strength, elongation at break, and toughness were improved by the addition of PEG-TOCN (≤2.5% w/w).

  ↳ Different behavior with conventional nanocellulose/polymer composites. Interfacial PEG layers contributed energy dissipation of CTA matrix.

- Phenomena occur at the TOCN/CTA interface
  - Stress transfer
  - Deformation or slippage
  - Stress relaxation
  - Fracture
  - Light scattering
  - Thermal diffusion or thermal transfer

NEXT The contribution of interfacial structures

Contents

General introduction

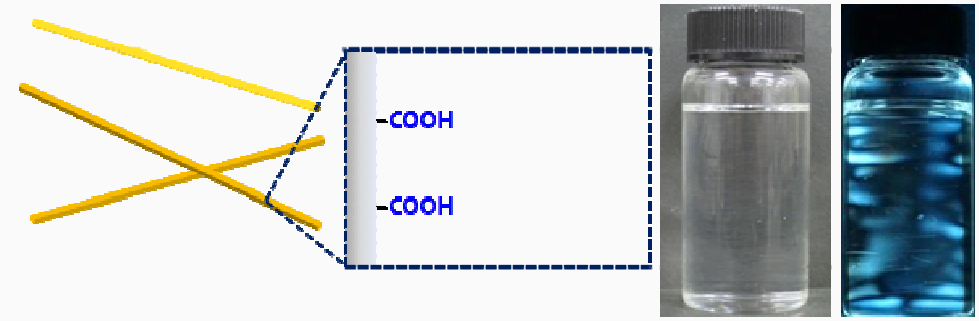
Preparation of PEG-TOCN/CTA composites

Interfacial layer thickness vs. material properties

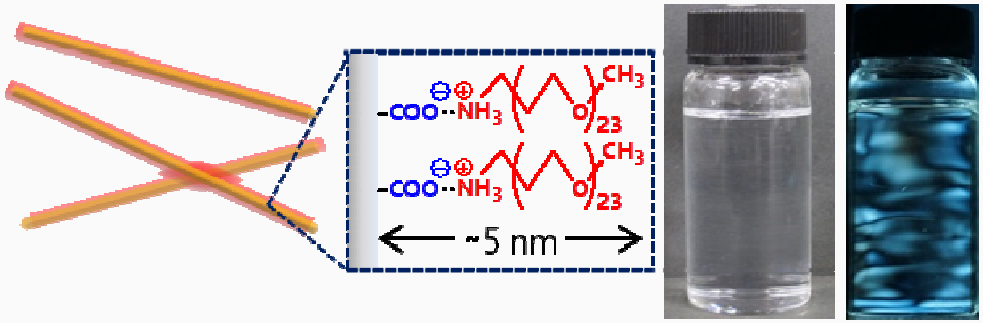
Grafting density vs. material properties

Conclusion

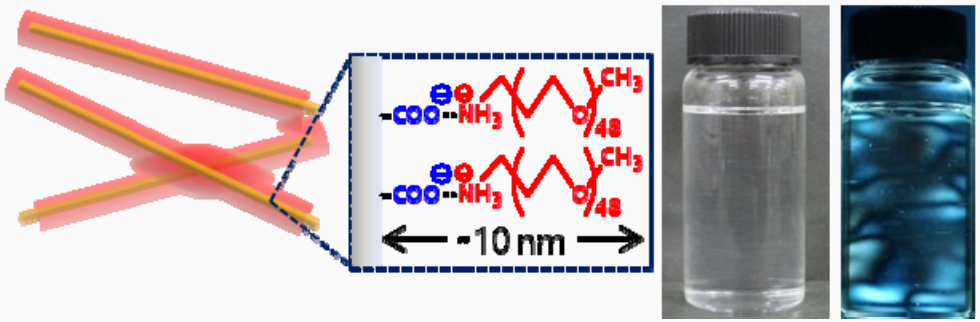
Interfacial layer thickness vs. material properties



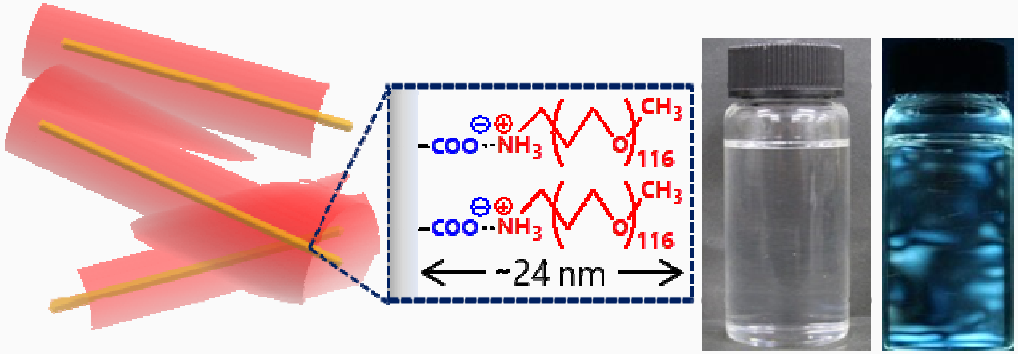
P_0-T (PEG M_w = 0)



P_{23}-T (PEG M_w = 1000)



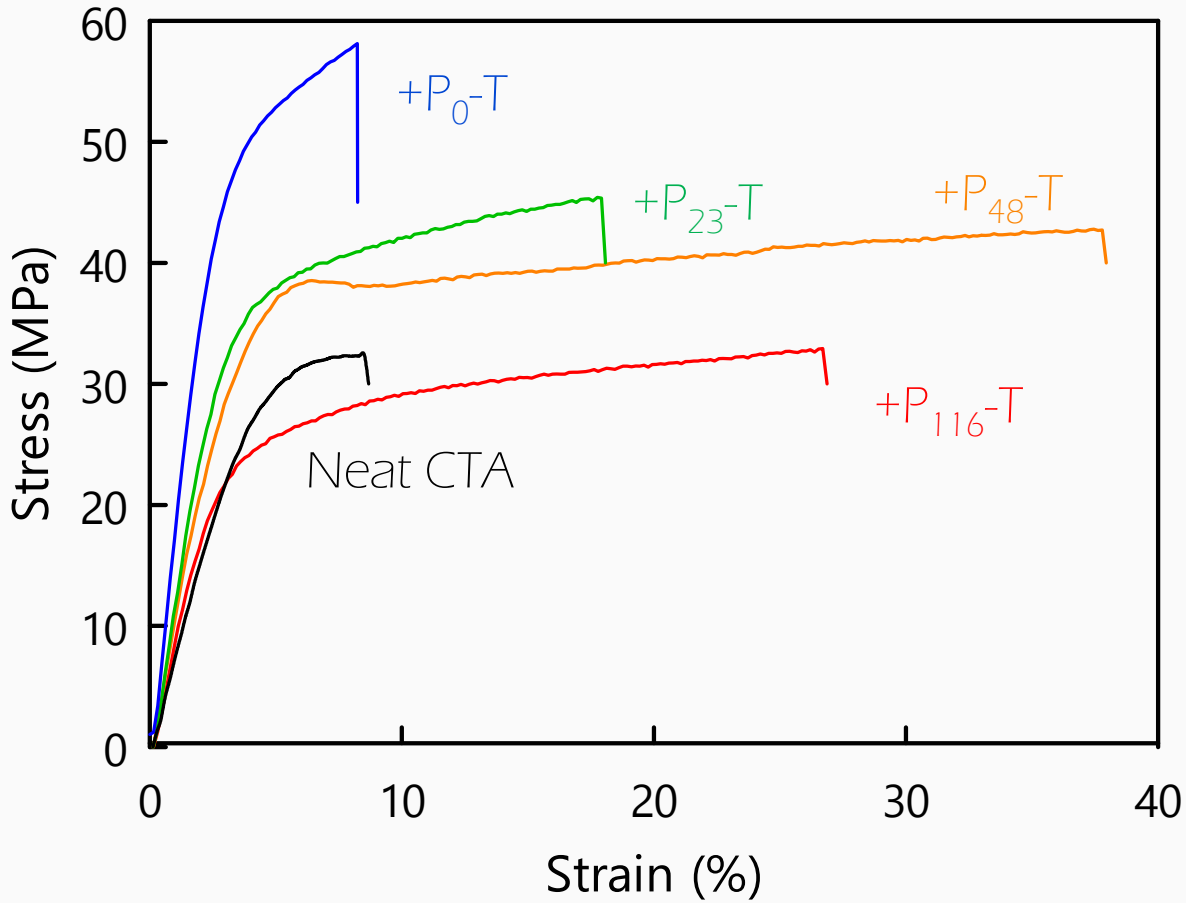
P_{48}-T (PEG M_w = 2000)

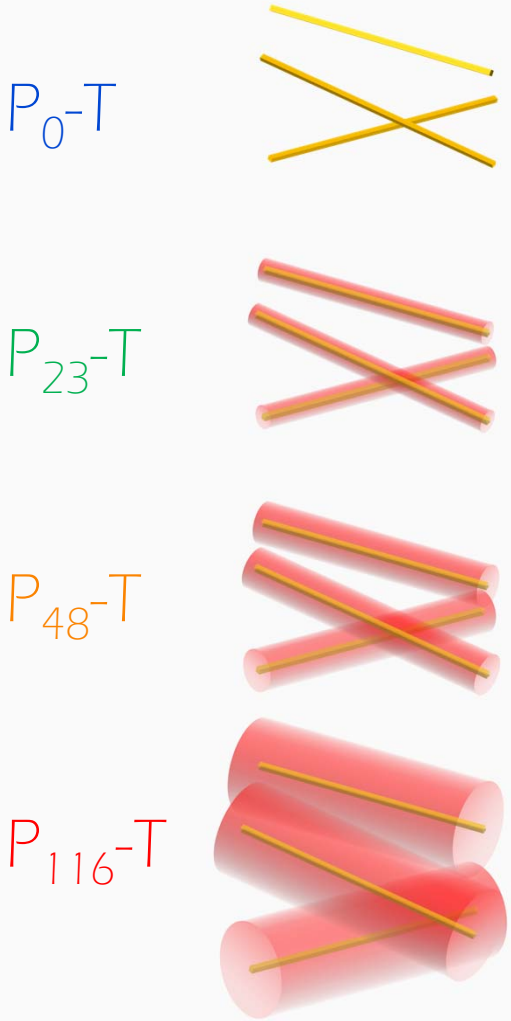


P_{116}-T (PEG M_w = 5000)

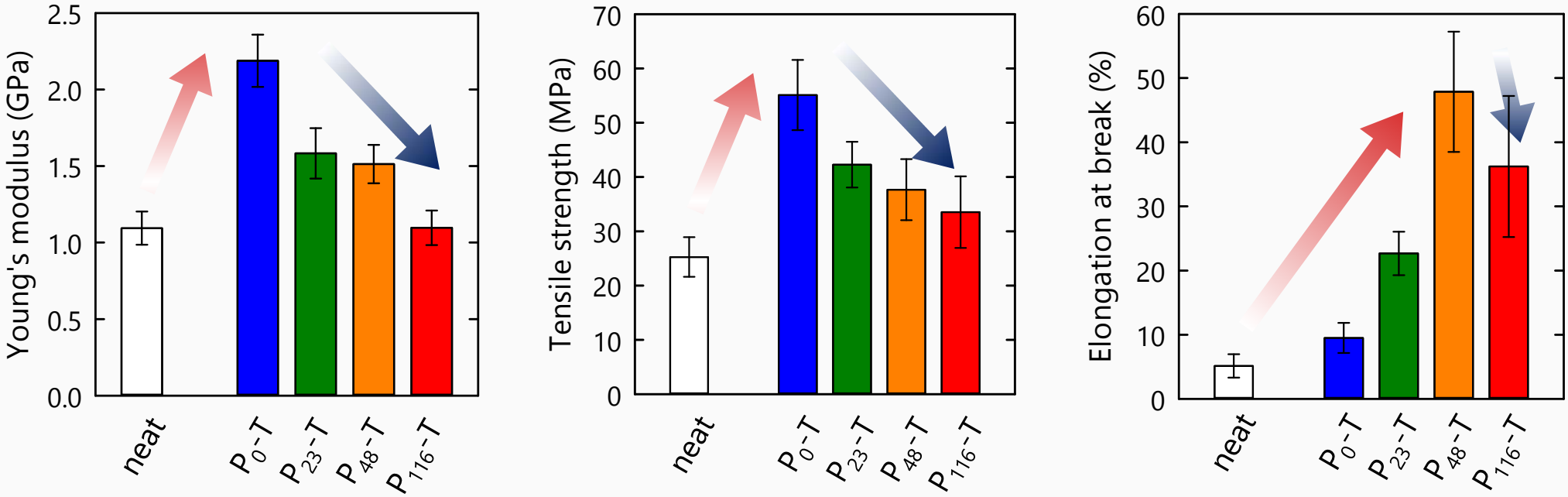
- Casting solvent: *N,N*-dimethylacetamide
- TOCN content: $\frac{TOCN}{TOCN+PEG+CTA} \times 100$ = 2.5 (% w/w)

Interfacial layer thickness vs. mechanical properties





Interfacial layer thickness vs. mechanical properties



- **Thin** interfacial layer: stiff and strong
  Thick interfacial layer: ductile and tough
- Interfacial layer with appropriate thickness was important for combining stiffness, strength, and toughness

- TOCN/CTA composites with thin interfacial layer: stiff and strong
  thick interfacial layer: ductile and tough

P48-T/CTA composites showed the highest toughness.

↳ Thick PEG layers may induce fracture at the interfacial layers.

Designing the interfacial layer with appropriate thickness is required to improve modulus, strength, ductility, and toughness.

Contents

General introduction

Preparation of PEG-TOCN/CTA composites

Interfacial layer thickness vs. material properties

Grafting density vs. material properties

Conclusion

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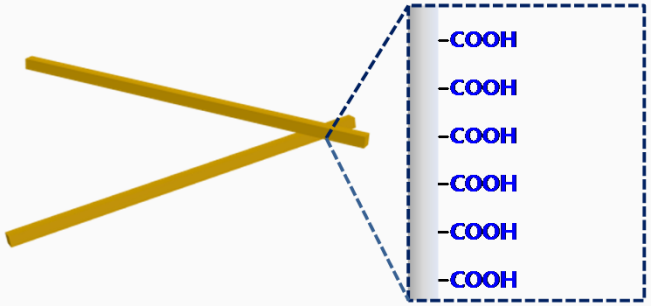
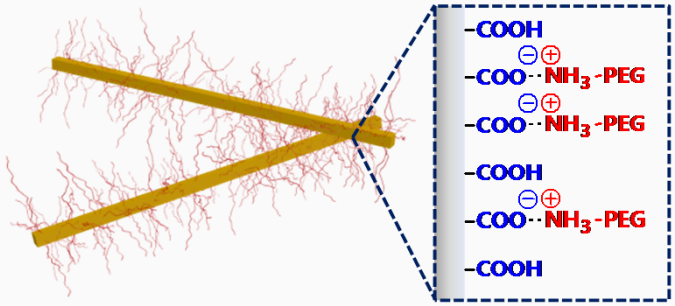
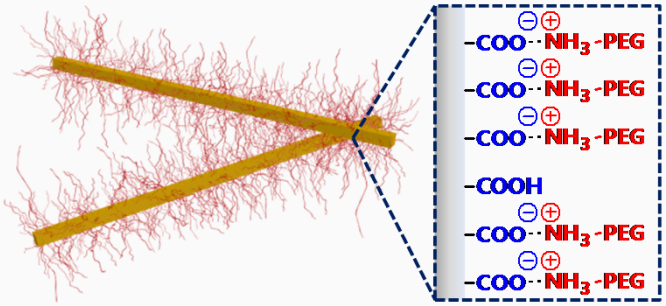
Low grafting density

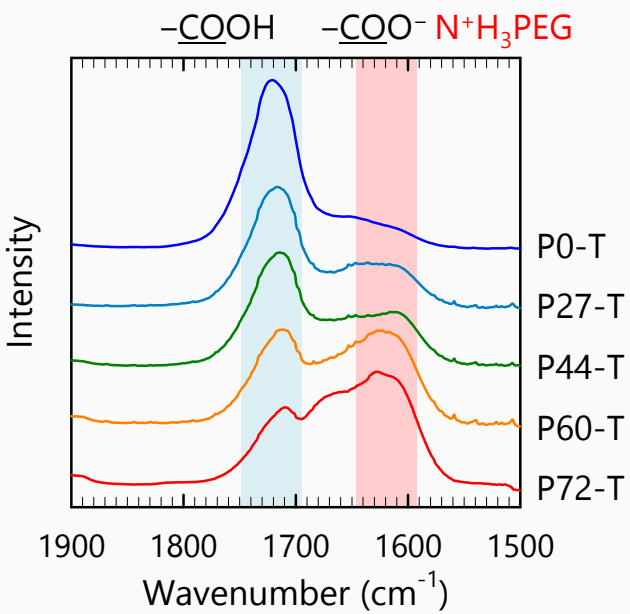


Intermediate grafting density



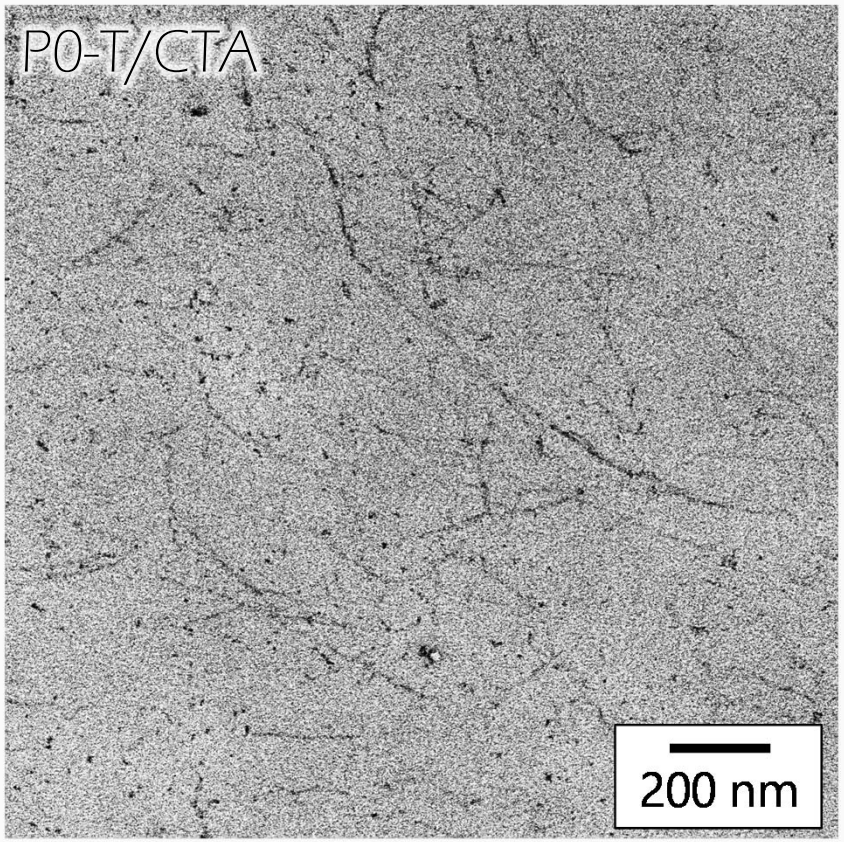
High grafting density

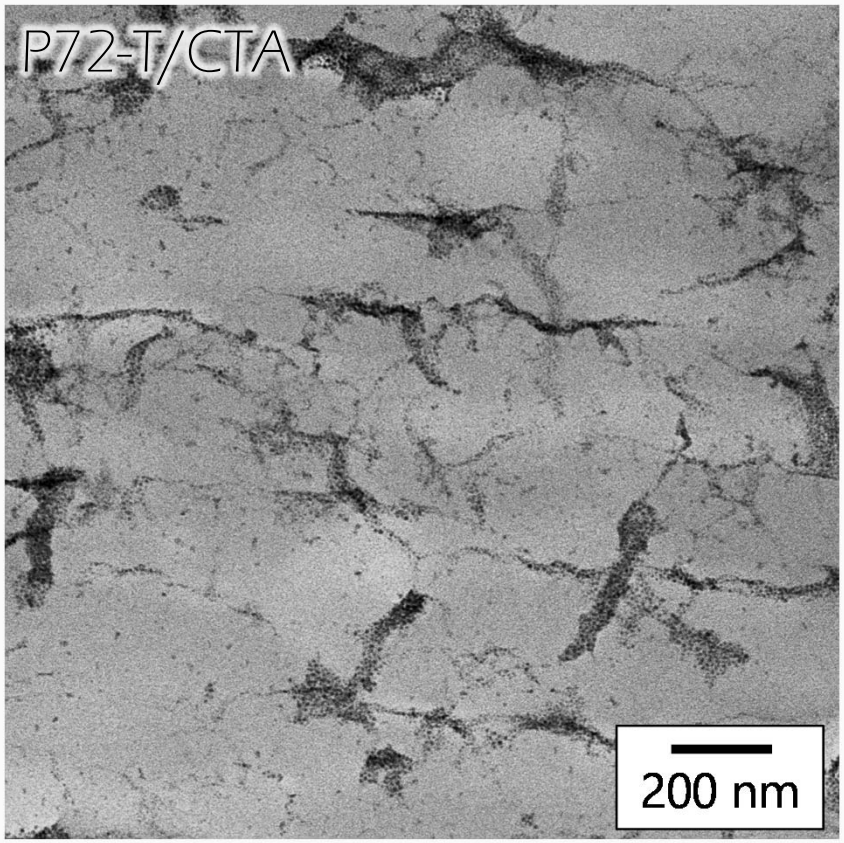




- Carboxy group content of TOCN: 1.78 mmol/g
  0, 27, 44, 60, 72% of surface carboxy groups were grafted with PEG-NH_2.
  →PX-T (X: grafting ratio)
- Molecular weight of PEG-NH_2: ~2000
- TOCN content: 2.5% w/w
- Casting solvent: *N,N*-dimethylacetamide

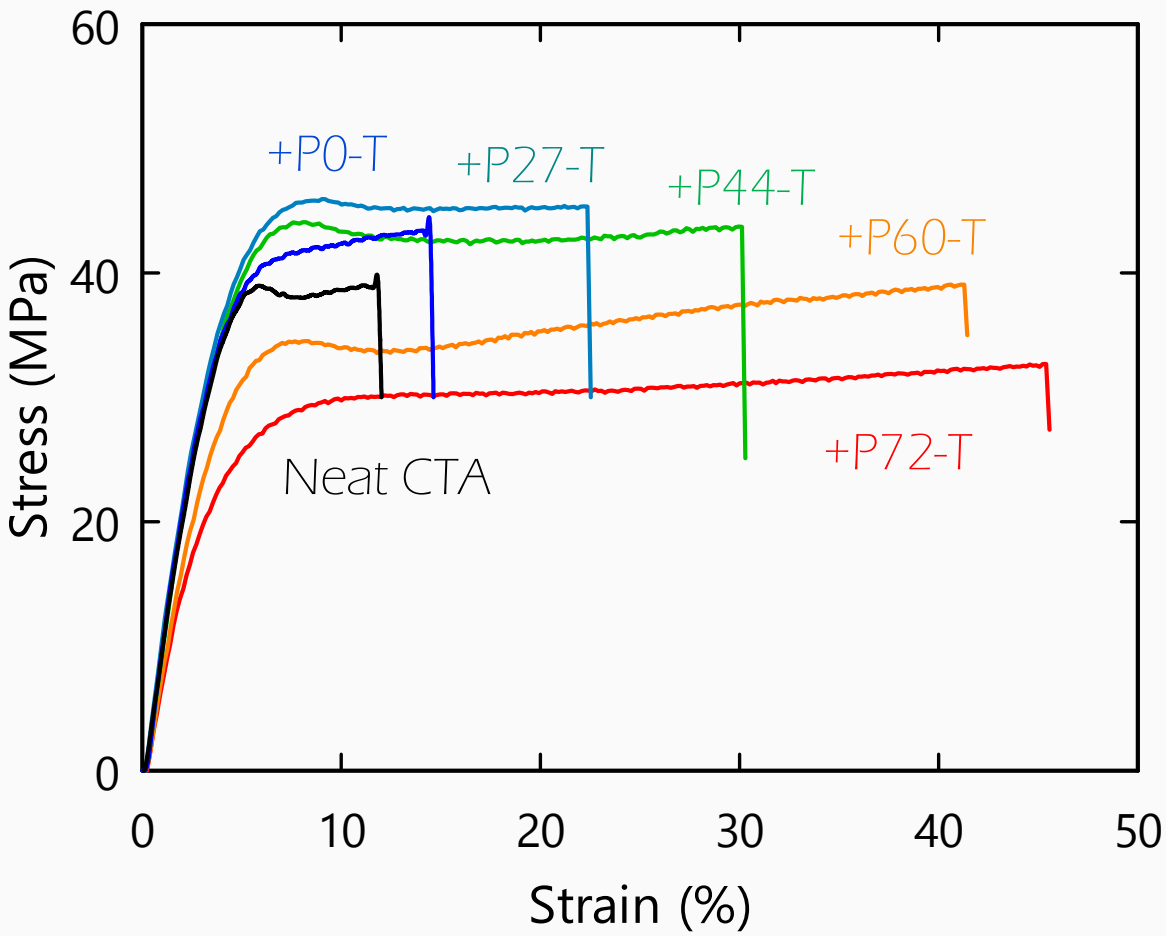
TEM observation

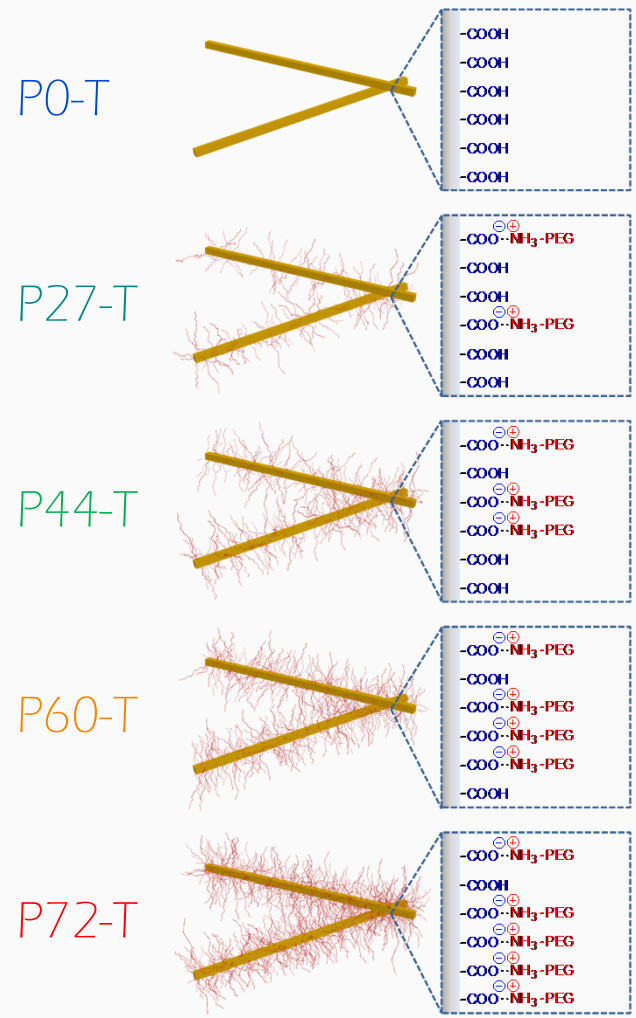




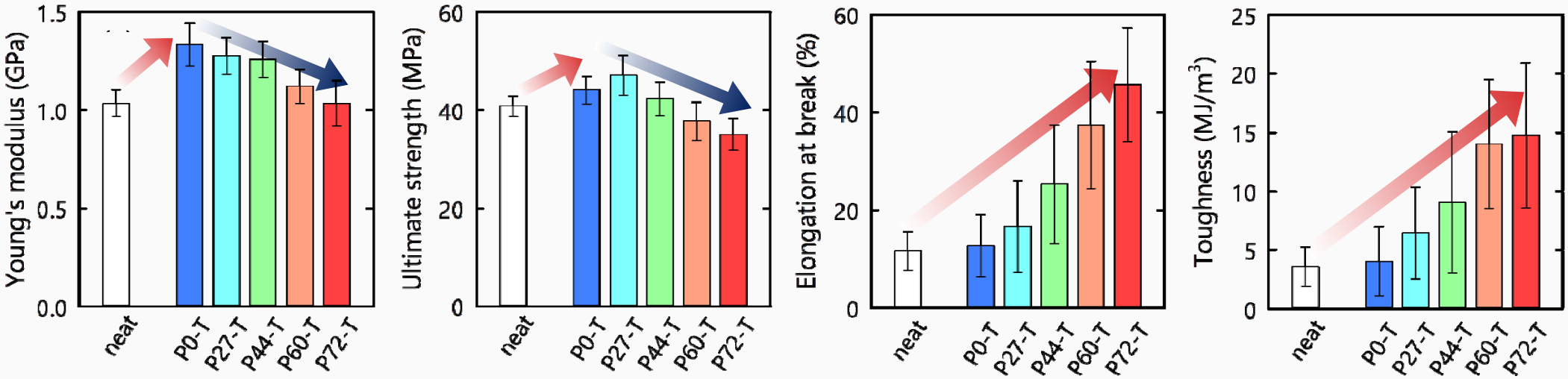
TOCNs were individually dispersed with/without surface modification

Grafting density vs. mechanical properties



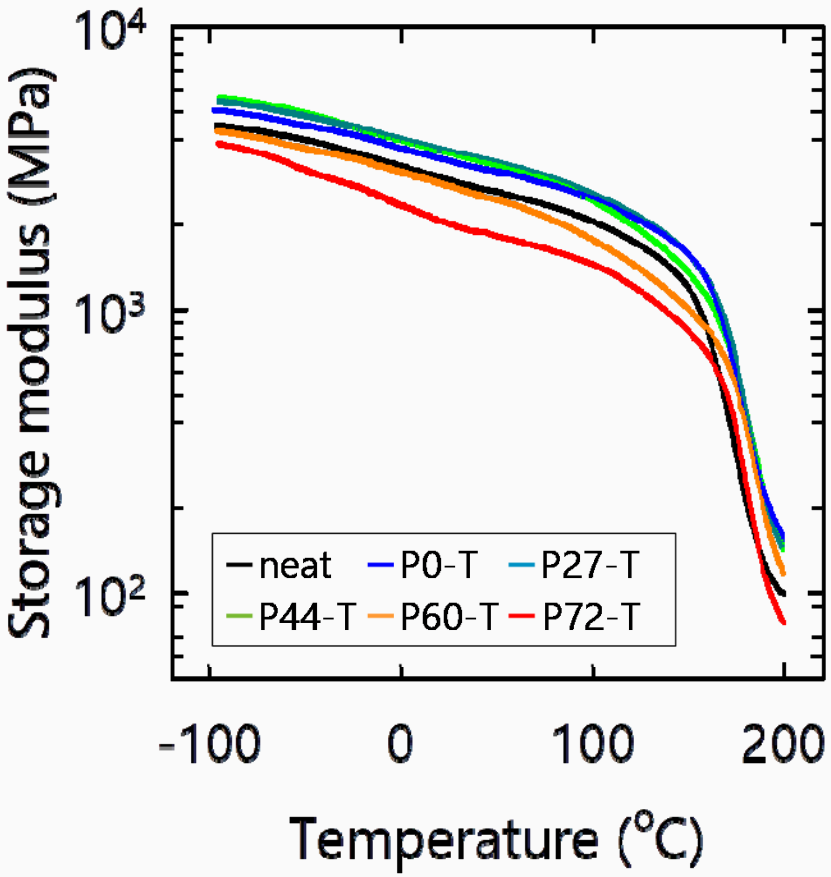


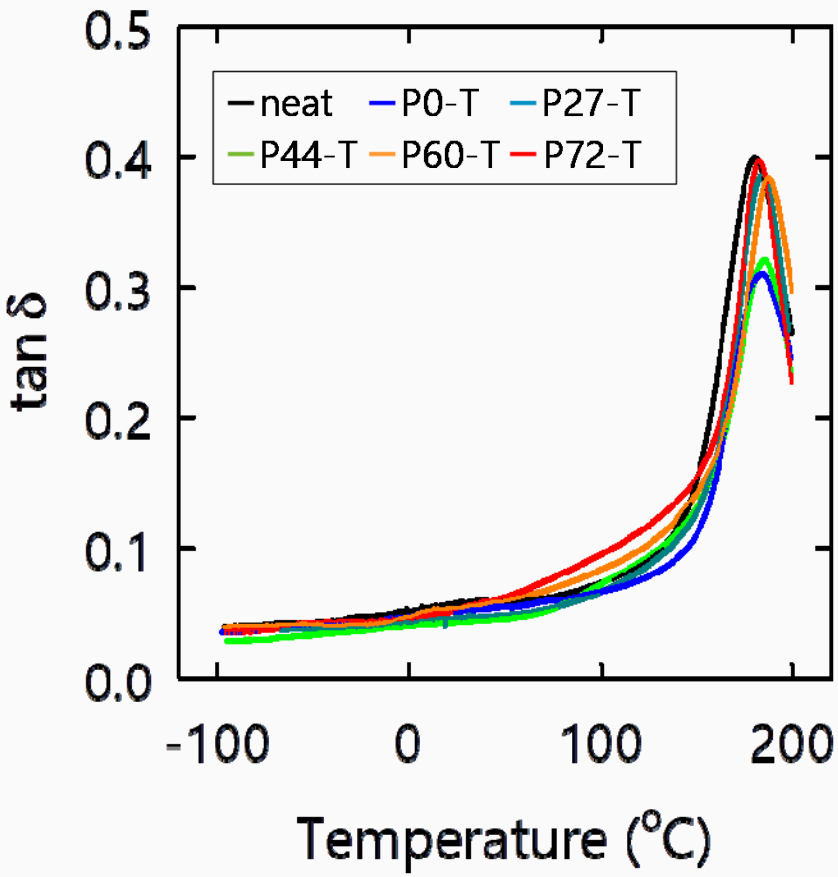
Grafting density vs. mechanical properties



- **Low** grafting density: stiff and strong
  High grafting density: ductile and tough
- Designing the grafting density is required to improve stiffness, strength, and toughness of the composites

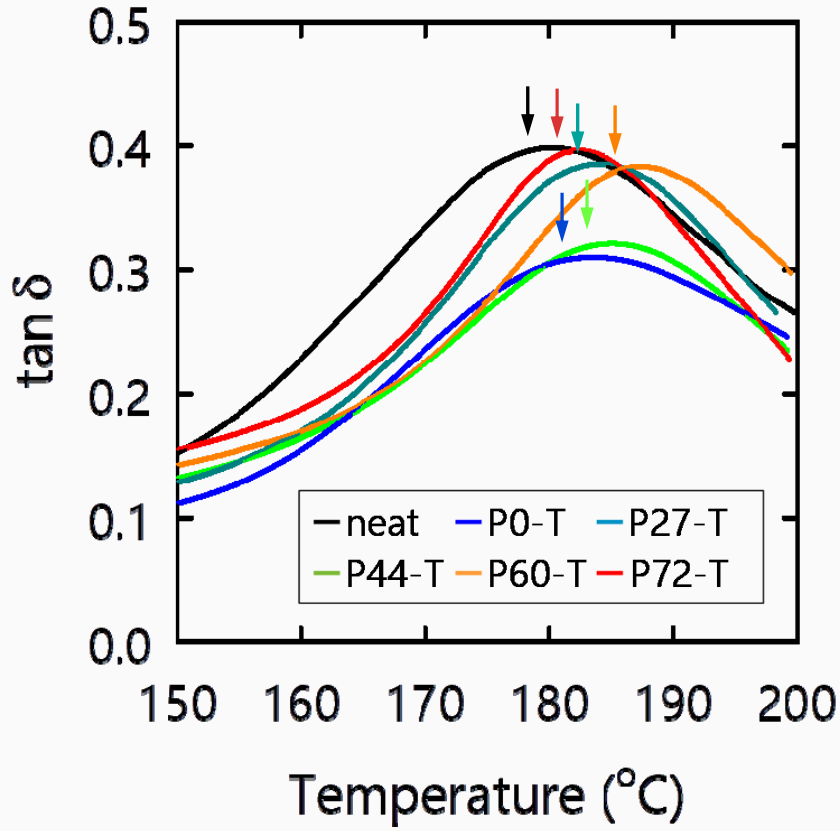
Grafting density vs. dynamic mechanical properties





Grafting density vs. dynamic mechanical properties

	T_g (°C)
neat CTA	180.3 ± 2.7
P0-T	183.2 ± 2.8
P27-T	184.3 ± 1.8
P44-T	185.1 ± 0.8
P60-T	186.7 ± 0.7
P72-T	184.1 ± 2.7



Glass transition temperature of CTA matrix was increased;

change in compatibility between grafted-PEG and CTA?

- TOCN/CTA composites with low grafting density: stiff and strong
  high grafting density: ductile and tough

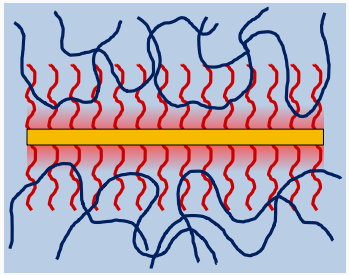
  Dense grafted layer had a strong plasticizing effect.

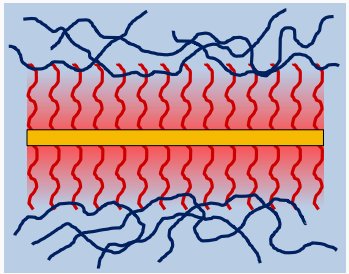
  Appropriate grafting density is required to obtain good reinforcing effect.

- Glass transition temperature of CTA matrix was slightly increased by the addition of PEG-TOCN.

  Grafted-PEG chains had different characteristics with free PEG chains.

  Compatibility between PEG and CTA was affected by grafting?





Contents

General introduction

Preparation of PEG-TOCN/CTA composites

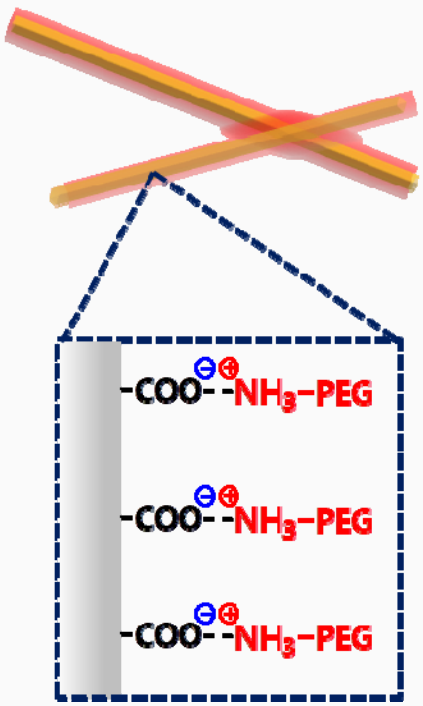
Interfacial layer thickness vs. material properties

Grafting density vs. material properties

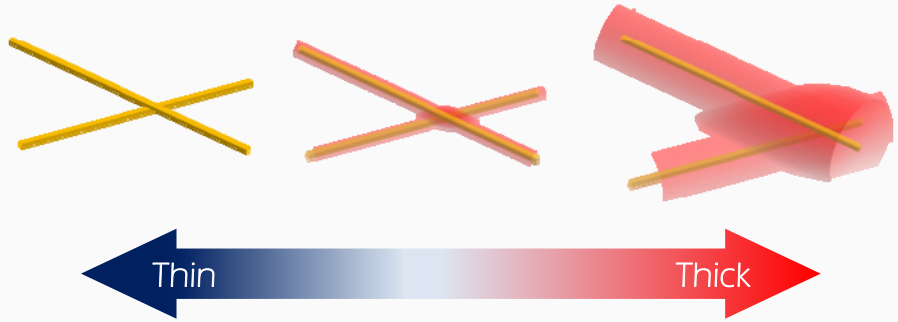
Conclusion

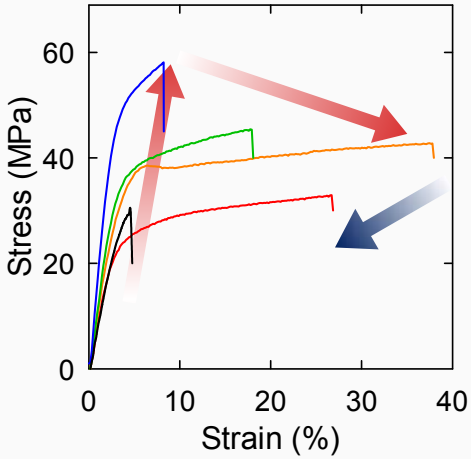
Conclusion

Interfacial structure vs. material properties

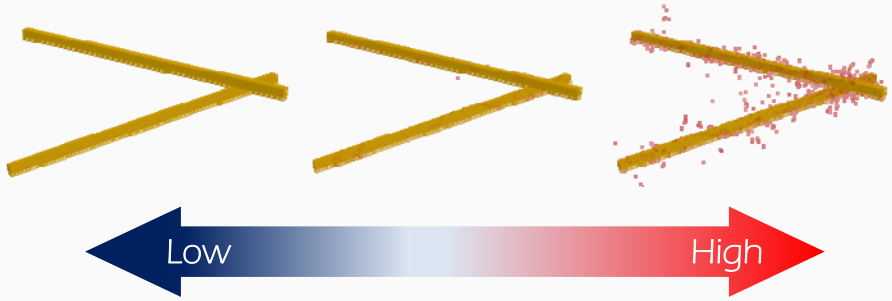


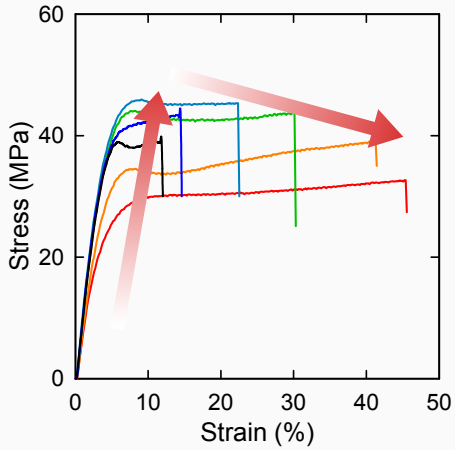
Interfacial layer thickness





Grafting density





- PEG-TOCN/CTA composites were stiff, strong, and tough.
- Interfacial layer thickness and grafting density affected reinforcing effect of TOCN.

Thank you

PRESENTED BY

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