# Structures and applications in fluorescent paper of cellulose derivatives/Eu(Tb) nanocomplexes

Huiming Liu; Jun Ye; Jian Xiong

South China University of Technology

Jun Ye
Professor
State Key Laboratory of Pulp and Paper Engineering

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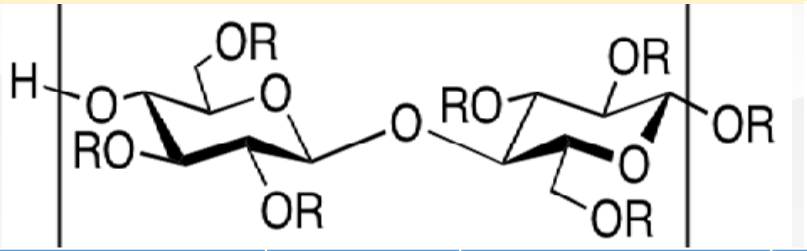
# 01

# Structures

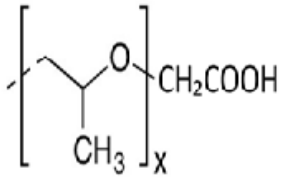
# Experimenetal

## ligand (CD): carboxymethyl cellulose (CMC), hydroxypropyl carboxymethyl cellulose (HPCMC)

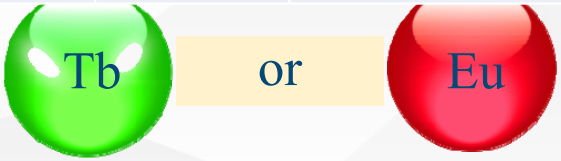



**CMC:** R= -H, $-CH_2COOH$

**HPCMC:** R= -H, $-CH_2COOH$ or



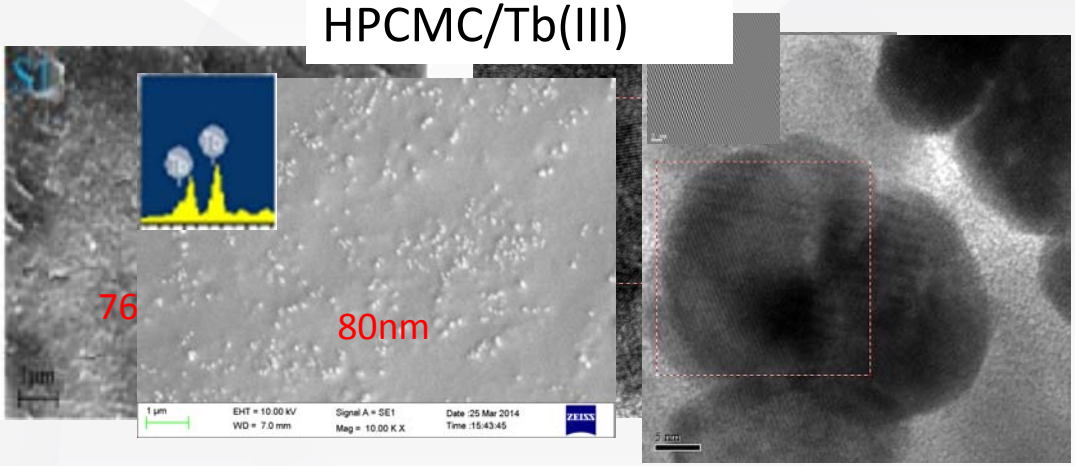

| Sample | CD | $RE^{3+}$ | n(CD):n(RE) | pH | T/℃ | t/min |
|---|---|---|---|---|---|---|
| CT | CMC | $Tb^{3+}$ | 15:1 | 7 | 70 | 35 |
| CE | CMC | $Eu^{3+}$ | 1.65:1 | 7 | 70 | 35 |
| HT | HPCMC | $Tb^{3+}$ | 15:1 | 7 | 70 | 35 |
| HE | HPCMC | $Eu^{3+}$ | 20:1 | 7 | 70 | 35 |

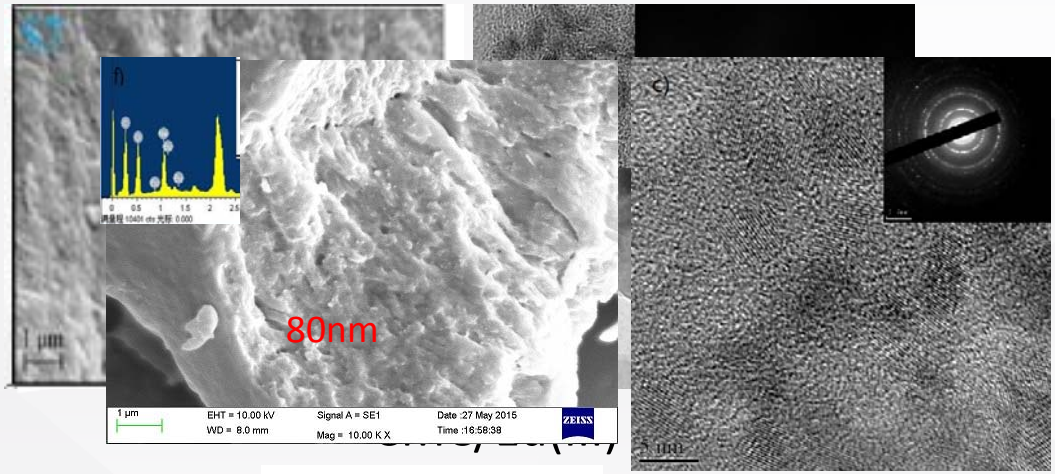



Fluorescence centers

# SEM & TEM

HPCMC/Tb(III)




HPCMC/Eu(III)

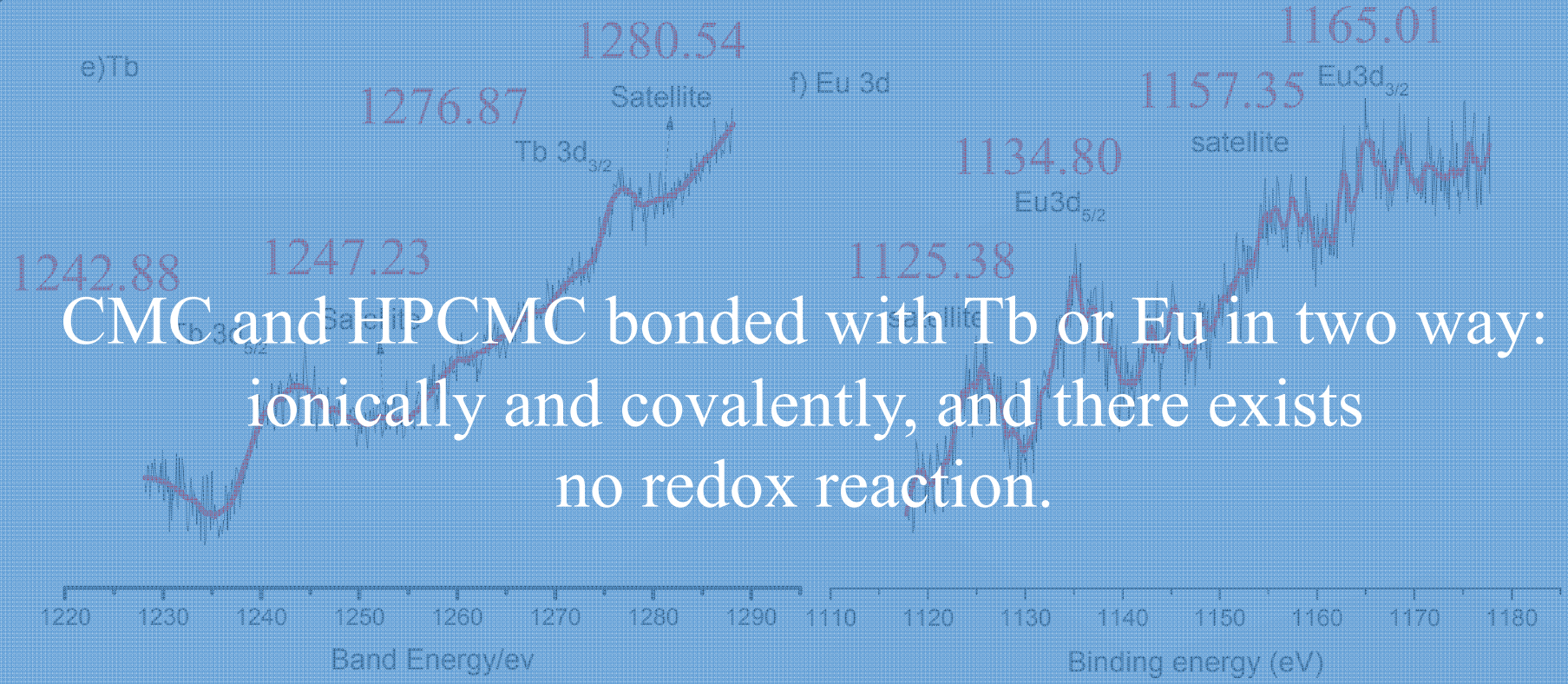
inset: the magnified image of the TEM of the products.

- Similar spherical particles and spheroid shape diameters <100nm on SEM
- the size around 13nm on TEM

there were no visible changes of these suspensions for a month.

The nanoscale size of the composites resulted in their good stability and dispersion in suspensions.

# XPS of CMC—Tb ion and Eu ion




CMC and HPCMC bonded with Tb or Eu in two way: ionically and covalently, and there exists no redox reaction.

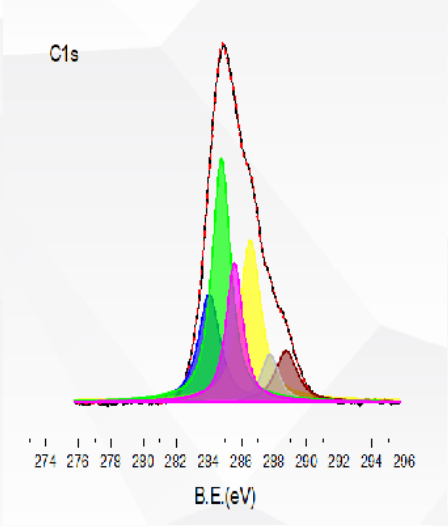
Tb exists in the form of $Tb^{3+}$

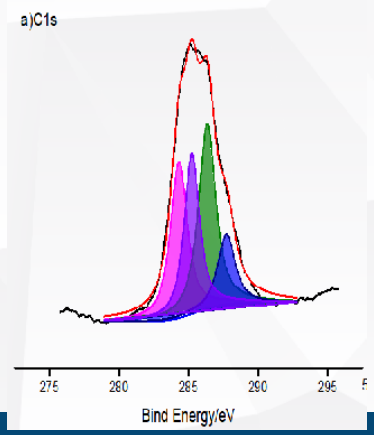
Eu exists in the form of $Eu^{3+}$.

Polymer Composites. 38：E498-E507, 2017
Carbohydrate Polymers. 135: 57–63, 2016

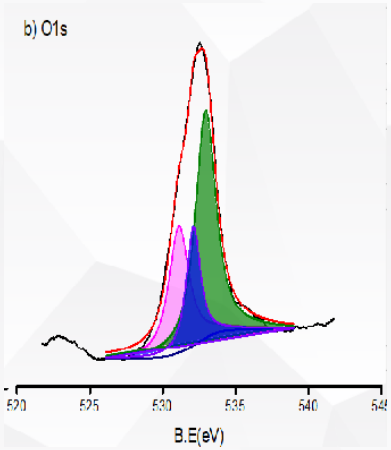
# XPS—C1 (CMC/Eu)

| | CMC C1s(eV) | S C1s(eV) |
|---|---|---|
| ➢ C-C or C-H | 284.36 | 284.01 |
| ➢ C-OH | 285.22 | 284.78 |
| ➢ O-C-O, C=O | 286.33 | 285.60 |
| ➢ C (in $COO^-$) | 287.70 | 286.61 |
| | - | 287.76 |
| | - | 288.72 |

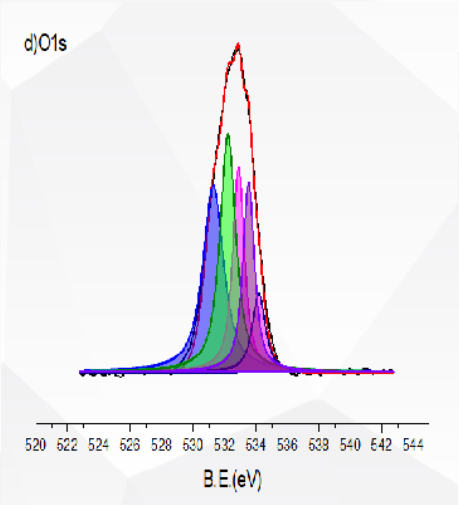


# XPS— O1(CMC/Eu)




| | CMC O1s(eV) | S O1s(eV) |
|---|---|---|
| ➢ C-OH | 532.12 | 531.18 |
| ➢ C-O-C | 532.16 | 532.24 |
| | | 532.92 |
| ➢ C=O | 532.93 | 533.50 |
| | | 534.16 |



# XPS of HPCMC/Tb

***The C1s and O1s Binding Energy of HPCMC and HPCMC/Tb***

eV)

90

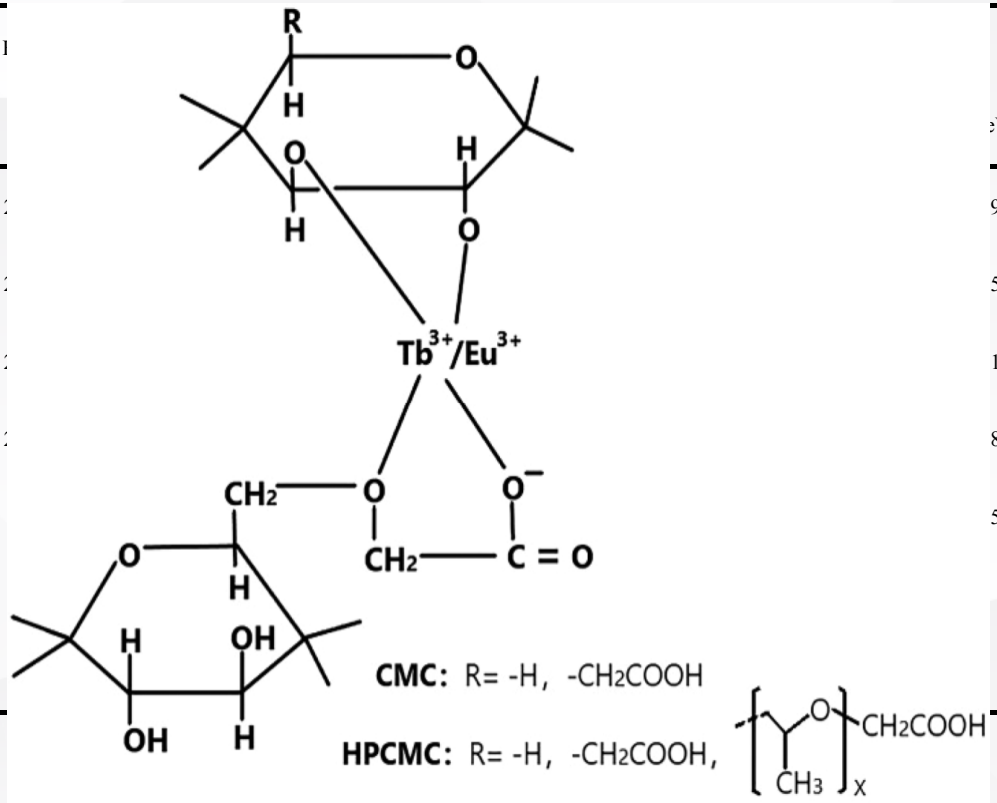
53

17

88

51

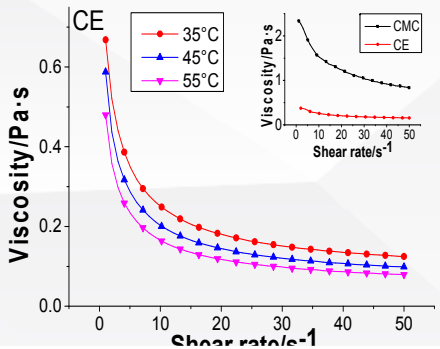
1.55 nm

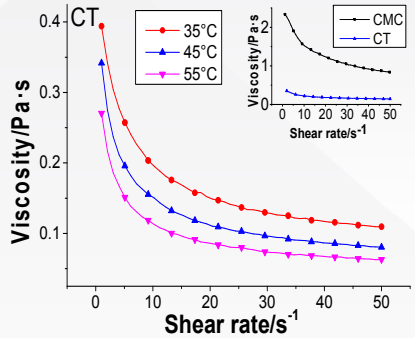


# 02

# Rheological Properties

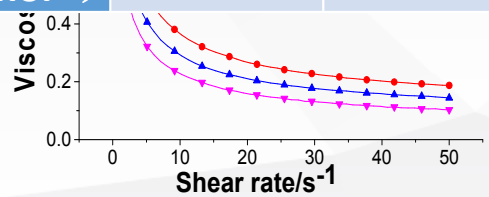
# rheology

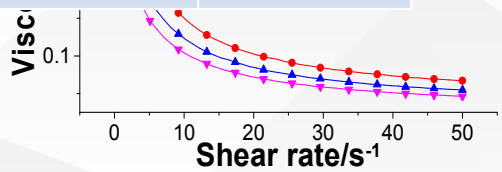



$$\ln \mu_0 = \ln B - Ea/RT$$

| | CE | CT | HE | HT |
|---|---|---|---|---|
| Ea（KJ·mol$^{-1}$） | 1.5964 | 2.5193 | 1.6047 | 1.4218 |




The relationship between the viscosity and shear rate of the composites suspensions at different temperatures
(inset: the relationship between the viscosity and shear rate of samples at 25℃)

- remain the shear-thinning properties of CMC and HPCMC
- the viscosities of the composites suspensions are lower than CMC or HPCMC solution
- a strong dependency of steady state shear viscosity of the composites suspensions upon temperature
- temperature has the greatest effect on CT suspension

CT, CE, HT, and HE are feasible to be used in paper-coating process during 35-55℃

# rheology

Cross model $$\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = \frac{1}{1 + (K \cdot \gamma)^{1-n}}$$

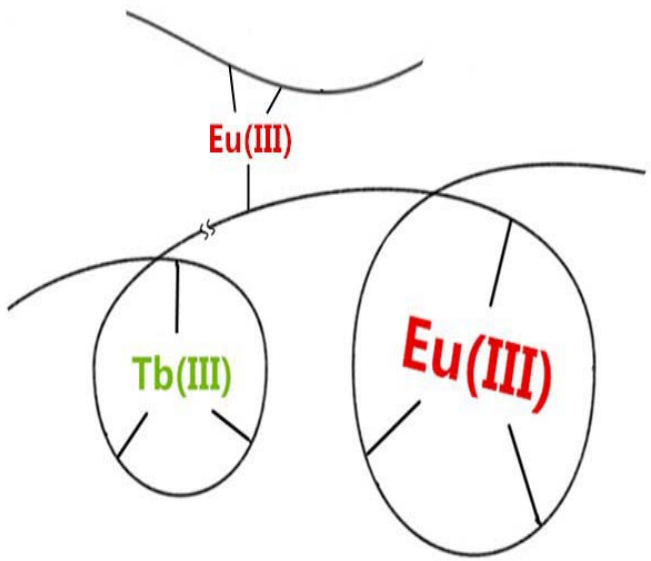
| Sample | | 35℃ | 45℃ | 55℃ |
|---|---|---|---|---|
| CMC/Eu(III) | n | 0.560 | 0.540 | 0.530 |
| | K | 0.703 | 0.598 | 0.492 |
| | $\mu_0$(Pa·s) | 0.3693 | 0.3055 | 0.2514 |
| CMC/Tb(III) | n | 0.640 | 0.620 | 0.620 |
| | K | 0.445 | 0.360 | 0.278 |
| | $\mu_0$(Pa·s) | 0.2669 | 0.2065 | 0.1566 |
| HPCMC/Eu(III) | n | 0.507 | 0.550 | 0.510 |
| | K | 1.003 | 0.840 | 0.714 |
| | $\mu_0$(Pa·s) | 0.5329 | 0.4332 | 0.3622 |
| HPCMC/Tb(III) | n | 0.510 | 0.500 | 0.500 |
| | K | 0.453 | 0.389 | 0.325 |
| | $\mu_0$(Pa·s) | 0.2343 | 0.1966 | 0.1663 |

- n of individual suspensions remain constants basically.
- n of the suspensions involved HPCMC change more with temperature, compared to that with CMC and with the same RE ions

short side chains on HPCMC could react with $Eu^{3+}$ or $Tb^{3+}$

# rheology

| Sample | | 35℃ | 45℃ | 55℃ |
|---|---|---|---|---|
| CMC/Eu(III) | n | 0.560 | 0.540 | 0.530 |
| CMC/Tb(III) | | | | |
| HPCMC/Eu(III) | | | | |
| HPCMC/Tb(III) | n | 0.510 | 0.500 | 0.500 |
| | K | 0.453 | 0.389 | 0.325 |
| | $\mu_0$(Pa·s) | 0.2343 | 0.1966 | 0.1663 |




- $\mu_0$ of the suspensions of composites with Tb(III) is smaller than these with Eu(III)

$Tb^{3+}$ has smaller radius of ions than $Eu^{3+}$, so the chains of composites with Tb(III) become more compacted into smaller dimensions

# rheology

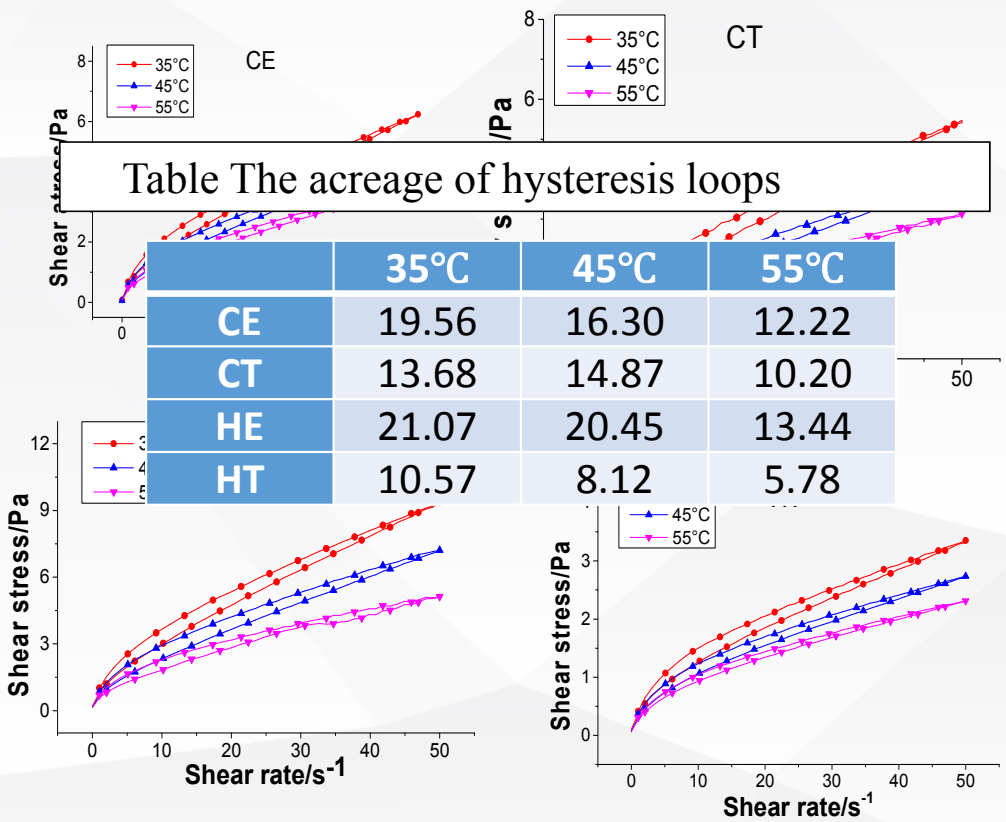



Table The acreage of hysteresis loops

| | 35℃ | 45℃ | 55℃ |
|---|---|---|---|
| CE | 19.56 | 16.30 | 12.22 |
| CT | 13.68 | 14.87 | 10.20 |
| HE | 21.07 | 20.45 | 13.44 |
| HT | 10.57 | 8.12 | 5.78 |

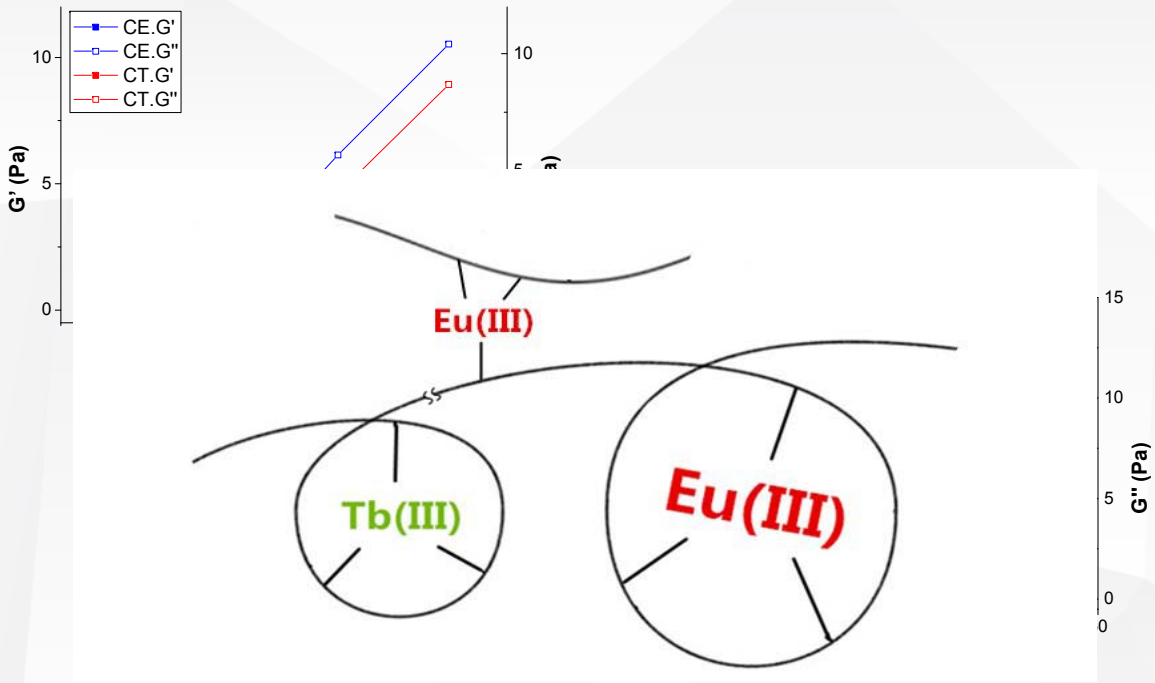
The hysteresis loops of the composites suspensions at different temperatures

- The composites suspensions had similar shape of thixotropic hysteresis loops with different acreage

these composites exhibit a viscosity-time relationship like CMC solution

CT, CE, HT, and HE as coating used in paper-coating process, and coating temperature could be adjusted according to the required thixotropy.

# rheology




The relationship between angular frequency and G′, G″ of the composites suspensions

- G″ of all composite suspensions is greater than G’ of them, which means the viscosity property is dominant compared to the elastic ones
- The G’ and G” of the suspensions with Eu(III) are higher than these of the suspensions with Tb(III).

more three-dimensional network structures in the composites with Eu(III)

# 03

# Fluorescent paper

# Fluorescent paper

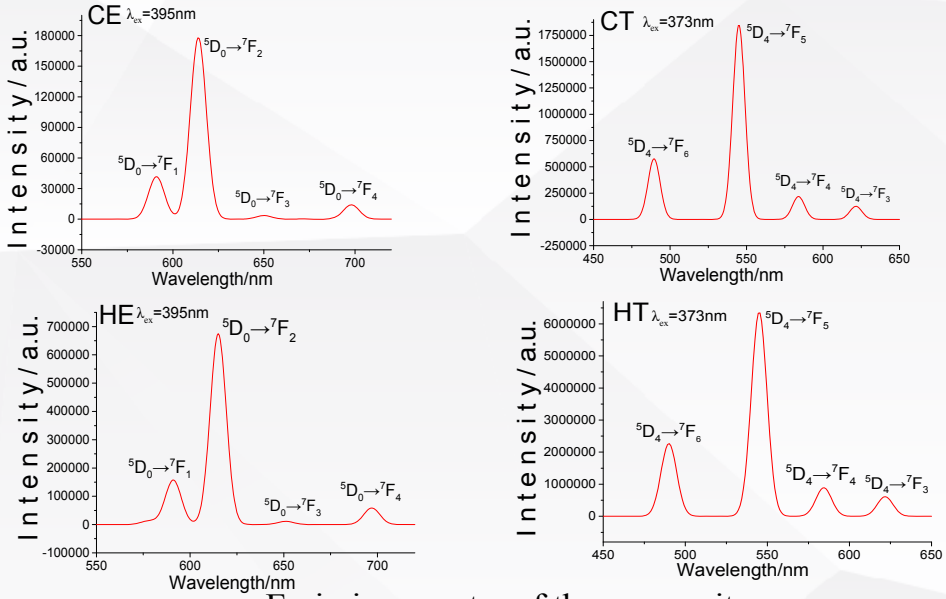
Photos under UV-light at 254nm
(from left to right: base paper sheet; pulp board; ordinary printing paper)

Preparation of the fluorescent paper sheets

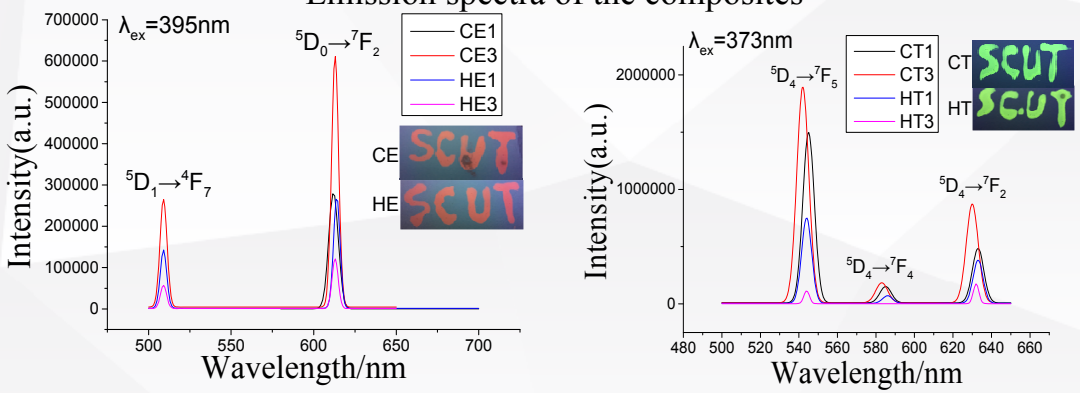
| Sample | Coating | Coating times | Coating weight(g / m$^2$) |
|---|---|---|---|
| CT1 | CT | 1 | 1.06 |
| CT3 | CT | 3 | 2.76 |
| CE1 | CE | 1 | 1.07 |
| CE3 | CE | 3 | 2.78 |
| HT1 | HT | 1 | 1.31 |
| HT3 | HT | 3 | 3.28 |
| HE1 | HE | 1 | 1.54 |
| HE3 | HE | 3 | 3.95 |
| control | - | 0 | 0 |

Photos under UV-light at 254nm

# PLE



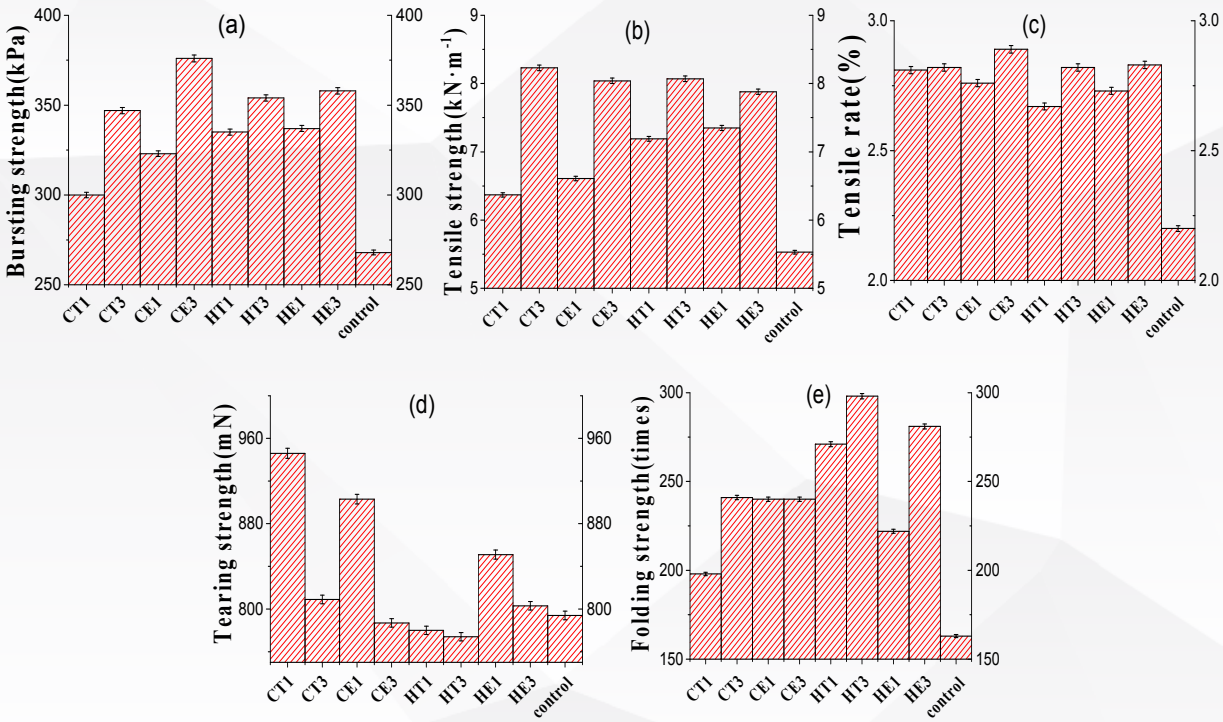

Emission spectra of the composites




Emission spectra of fluorescent paper sheets

- every kind of fluorescent paper still have characteristic emissions of $Tb^{3+}$ and/or $Eu^{3+}$, indicating that coating wouldn't change the fluorescence property of these composites
- The intensity of $^5D_0 \rightarrow {}^7F_2$ for $Eu^{3+}$ or $^5D_4 \rightarrow {}^7F_5$ for $Tb^{3+}$ of the fluorescent paper coated with CE and CT is greater than coated with HE and HT
- As the coating weight raises, there is a little red shift of emission of the fluorescent paper with $Eu^{3+}$, as well as an obvious blue shift of emission of fluorescent paper with $Tb^{3+}$

# Mechanical property of fluorescent paper




Mechanical properties of the fluorescent paper sheets: (a)Bursting strength; (b)Tensile strength; (c)Tensile rate; (d)Tearing strength; (e)Folding strength

- coatings can increase bursting strength, tensile strength, tensile rate and folding strength of these fluorescent paper sheets

both the large increase in tensile strength and toughness of the fluorescent paper

- Tear strength is higher for the fluorescent paper with lower coating weight.

# Mechanical property of fluorescent paper

Effect of different additives on mechanical properties of the coated paper

| Additives | Rate of increase (%) | | |
|---|---|---|---|
| | Bursting strength | Tensile rate | Tearing strength |
| CMC[1,2] | —— | —— | 1.69 |
| starch-acrylamide graft copolymer[3,4] | 20.7 | 34.5 | -0.3 |
| cationic starch[3,4] | 14.6 | 28.4 | 0.3 |
| our work | 11.9~40.3 | 21.4~31.4 | -2.5~19.14 |

- comparing with some common paper additives, the fluorescent composites exhibit a similar or even higher rate of increase on the mechanical properties of coated paper


1. *Cellulose.* **2014**, 21(6), 4569–4581
2. *Federal Reserve Bank of St. Louis Review*. **2007**, 89, 371-414
3. *Ind. Eng. Chem. Res.* **2014,** 53(36),13980-13988
4. *World Pulp and Paper.* **2002,** 21(2), 35-40

# Conclusions

- The suspension of composites shows a typical shears dilution behavior of pseudoplastic fluid. The viscosity is dependent on temperature, and it decreases with the increasing temperature. The storage modulus and loss modulus generally show a tendency to go up with the increase of the angular frequency.
- Coating will not change the internal structure and charge transfer of composites. Paper remains the characteristic fluorescence of composites after coating, making its applications possible
- Composites suspension's coating will bring about a promotion of some mechanical properties, such as folding strength, bursting strength and so on. Especially, there is an increase of both tensile strength and toughness of the fluorescent paper in this work, and the mechanical properties can be improved as the coating weight increases.

# 04

# Acknowledgements

# Acknowledgements

financial support provided by 制浆造纸工程国家重点实验室 State Key Laboratory of Pulp and Paper Engineering (Project 2016C12)

国家自然科学基金委员会 National Natural Science Foundation of China (Project 31270617).

THANK YOU
SUGGESTION