Hydrophobisation of pulp fiber with multilayering of saponified rosin and PAH

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Cellulose fiber has been used as raw material for papermaking because of its whiteness, self-bonding ability by hydrogen bond, chemical inertness, higher tensile stiffness, etc. With the abundance in nature and sustainability, the application fields of cellulose will be consistently increased. Nevertheless, its hydrophillicity can be one of obstacles to make green composite or packaging material with barrier property. Therefore, the modification of the surface property is required. LbL (Layer-by-Layer) multilayering technology can be adopted to make hydrophobic cellulose fiber. It is the technology that the surface of a substrate is layered by successive depositions of cationic polyelectrolyte and anionic polyelectrolyte (1). It is highly effective in modifying surface properties of material and has potential to be applied in various fields (2,3). In this study, we aimed to manufacture hydrophobic fiber by Layer-by-Layer multilayering with poly allyamine hydrochloride (PAH) and saponified rosin, and to investigate its effect on hydrophobicity and physical properties of paper.
Disintegrated hardwood pulp fibers were fractionated by using screen equipped with 400-mesh wire to remove colloidal and dissolved material. Then, the fibers were successively treated by PAH and saponified rosin to 9 layers, and handsheets with grammage of 100 g/m^2 were made from the treated fibers at each layering step. Adsorption of rosin on pulp fiber was examined by FT-IR and SEM. Hydrophobicity of the handsheet was evaluated by means of contact angle measurement and 900 s Cobb sizing degree. In addition, we evaluated mechanical properties of handsheets including tensile and tear strength.
The Cobb size values of the handsheets made from untreated fibers and PAH treated fibers as 1 layer were over 200 g/m^2 at 30 sec measurement. However, the resistance ability to water penetration of paper was remarkably improved after 2 layers. The 900 sec Cobb size degree of the paper was decreased with further layering of PAH and rosin, and it was maintained to 25 g/m^2 after 4 layers. High resistance to water penetration could be achieved by multilayering by PAH and rosin. In addition, the contact angle of sheet was increased up to 130 degrees. It seems that the cationic polyelectrolyte of PAH facilitates a high retention and desirable orientation of rosin by electrostatic bonding. When paper sheet was made of fibers with odd layer which PAH was adsorbed in the outermost layer, it showed a slight higher contact angle than sheet with rosin in the outermost layer. The bottom side of sheet showed higher contact angle and low Cobb value than top side of sheet. These seem to be caused by micro-roughness of PAH polyelectrolyte loop and fines.

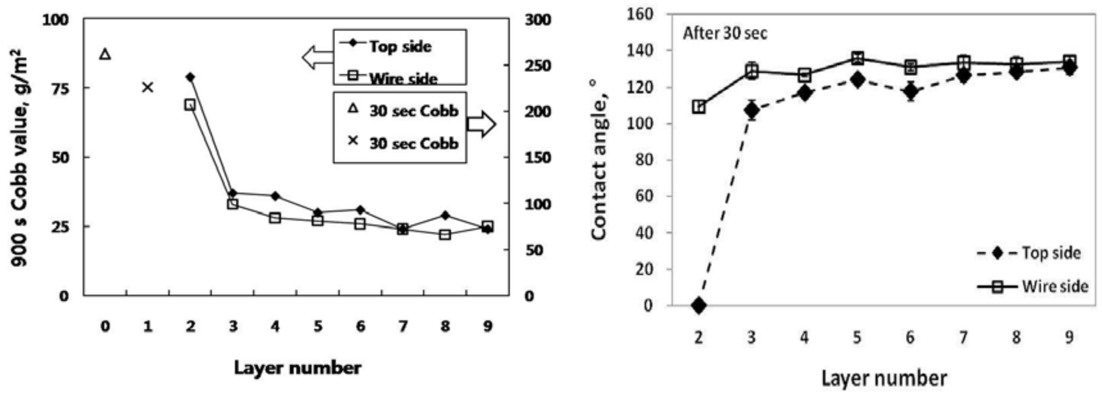

Fig. 1. Cobb sizing value (left) and contact angle (right) of handsheet with multilayering.

Despite the successive adsorption of hydrophobic materials by electrostatic interaction, tensile and tear strengths of paper increased with layering, especially at odd layer with PAH. In the case of even layer which rosin was in the outermost layer, the strength properties were maintained or a little decreased. The increase of tensile strength at the odd layer resulted from the increased conformability of fiber surface to bonding by the adsorbed polyelectrolyte and the increased adhesive force or joint strength between treated fibers as mentioned in earlier researches (4-6). The tear strength of sheet at odd number layer seemed to be increased due to the high friction between fibers induced by multilayer of polyelectrolytes.

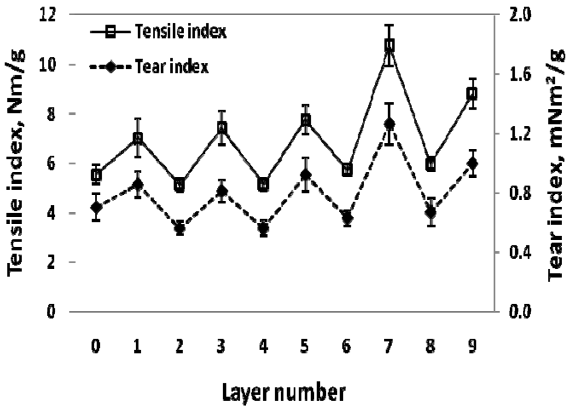

Fig. 2. Tensile and tear indices of sheet with multilayering.

From these results, it is suggested that LbL multilayering technology can be used to make hydrophobic paper, functional packaging material and bio-composite and also to give an extra function to paper.

Acknowledgement
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I. INTRODUCTION

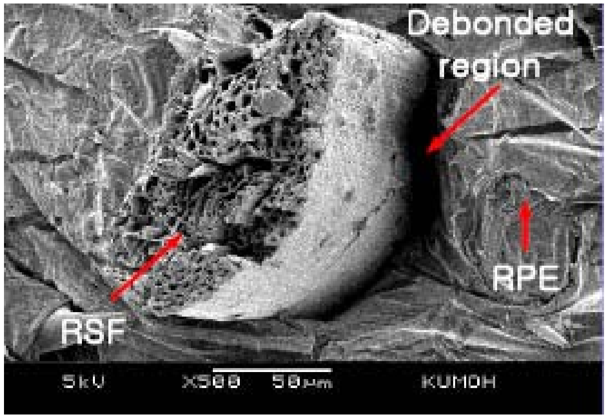
Introduction

- Cellulose fiber
  - Most abundant organic material in nature
  - High tensile strength
  - Water insoluble
  - Hydrophilic -> inherent bonding ability
  - Ability to absorb modifying additives
  - ...

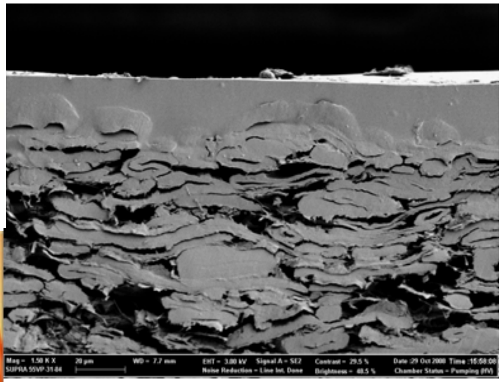
(G. Smook, Handbook for pulp & Paper Tehcnologists, 2002, TAPPI Press)

- Application of cellulose fiber
  - Paper, textile, food, film, biocomposite, etc.

- Biocomposite
  - Wettability and interfacial adhesion between natural fibers and polymer matrix
  - Modification of fiber surface characteristics
- Packaging paper
  - Barrier property



Cho,D.H. 2009



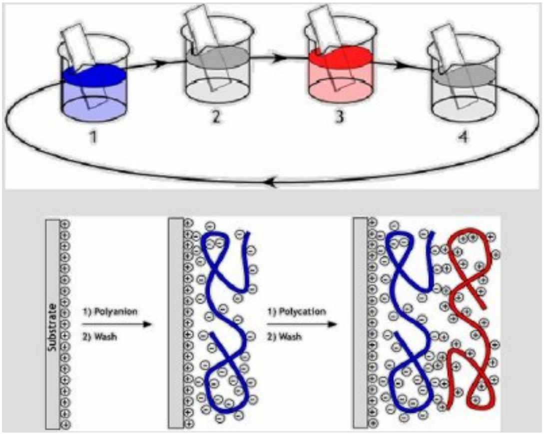
Kwon, H.-S & Youn, H.J. 2009

Hydrophobisation of fiber

- Sizing
  - Rosin, AKD, ASA
  - Temporary resistance of liquid penetration
  - Low/medium hydrophobicity
  - Disadvantages
    - acid papermaking (for rosin)
    - Sizing fugitivity, slippery surface (for AKD)
- Silylation
- Layer-by-layer multilayering

Layer-by-Layer multilayering

- G. Decher et al. (1992)
- Simple & versatile tool to modify substrate surface
- Application to pulp and paper
  - L.Wågberg
  - Y.Lvov
  - O.J. Rojas

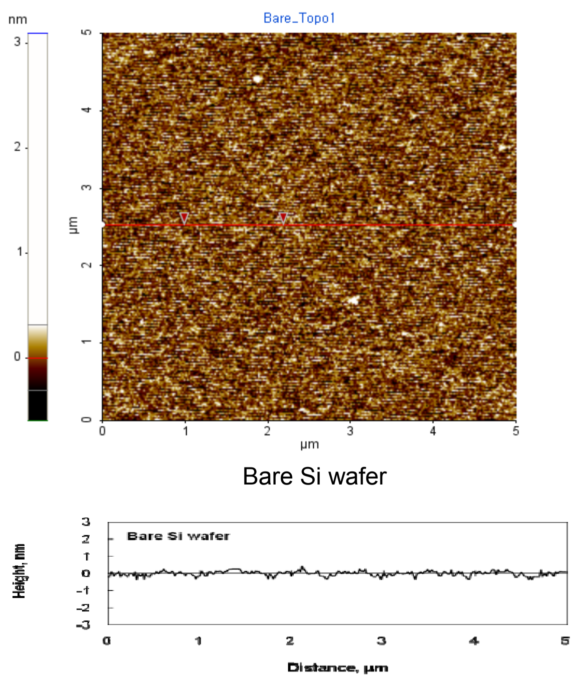


G.Decher, Science, 277:1232-1237 (1997)

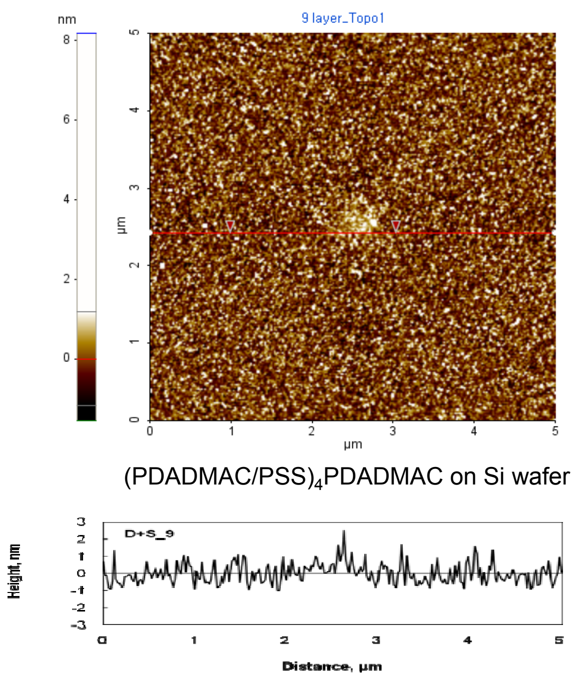
- Improvement of adhesive force between fibers

Layer-by-Layer multilayering

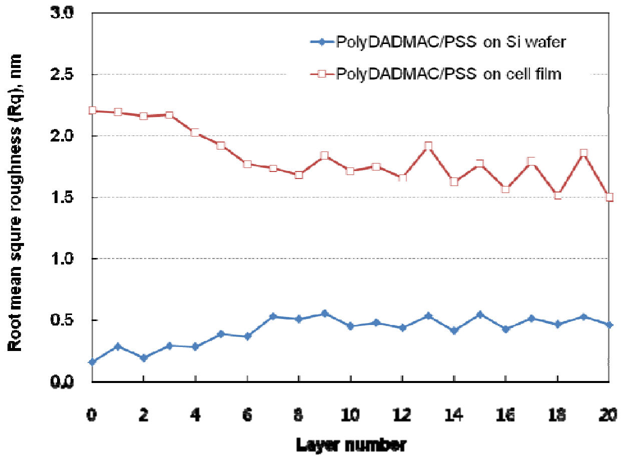
- A treatment to modify of surface chemistry and surface topology



Bare Si wafer



$(PDADMAC/PSS)_4$PDADMAC on Si wafer



(Chin, S.M. & Youn, H.J.,2010)

Objectives

- Manufacture of hydrophobic fiber using layer-by-layer multilayering technique
  - Cationic polyelectrolyte and anionic rosin
- Evaluation of hydrophobicity and physical properties of paper
  - Effect of layer number
  - Effect of drying condition
  - Effect of calendering

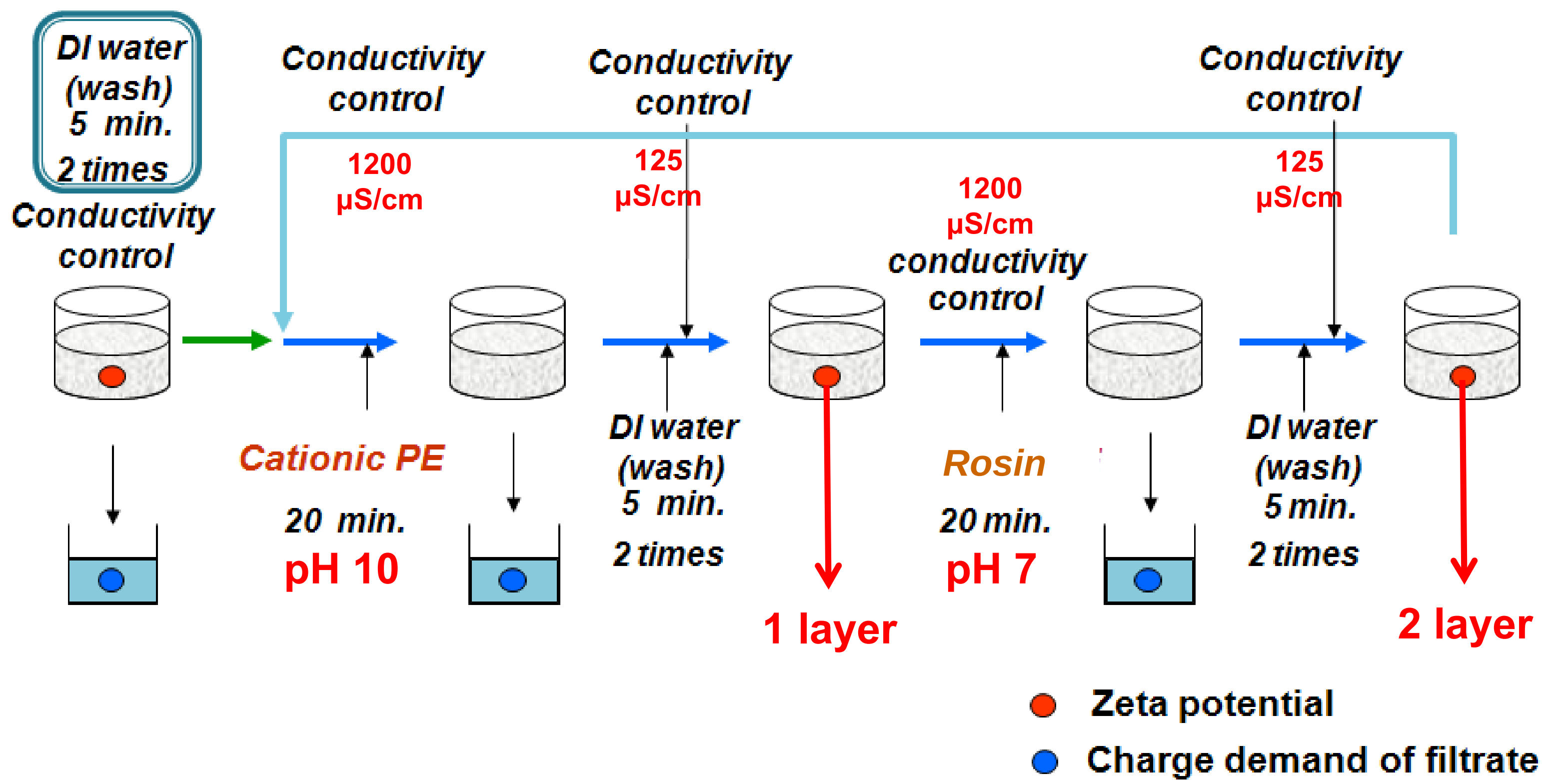
II. EXPERIMENTAL

Materials

- Hardwood bleached kraft pulp
  - Disintegrated in Valley beater
  - Colloidal and dissolved materials were removed by washing with the screen of 400-mesh wire
- Cationic polyelectrolyte and rosin

		Charge density (meq/g)	Molecular weight (g/mol)
Cationic	PAH (polyallylamine hydrochloride)	+ 10.72 @ pH 7 + 7.34 @ pH 10	~ 56,000
Anionic	Saponified rosin	- 0.26	

- Layer-by-Layer multilayering
  - ~ 9 layers
    - 1200 μS/cm, pH 10 (PAH, 0.2%), pH 7 (Rosin, 3.0%)



- Evaluation of electrochemical properties
  - Zeta potential of fibers
    - 125 μS/cm
    - SZP (Mütek Co.)

SZP

  - Adsorbed amount of PAH and rosin
    - Charge demand of filtrate after reaction
    - Adsorbed amount (mg/g) = $\frac{A-B}{A} \times \frac{C}{D}$
      - A : charge demand of the filtrate without pulp fiber, eq/L
      - B : charge demand of the filtrate, eq/L
      - C : oven dried weight of PAH or rosin, mg
      - D : oven dried weight of pulp fiber, g.

PCD

- Handsheet forming
  - Handsheet former
  - Grammage : 100±2 g/m^2
  - Calendering : 0, 50 kg_f/cm^2
  - Drying condition

	Drying	Heat treatment
Air	1 day @ 20˚C	x
Drum*	90 sec @ 120˚C	180 min @ 130˚C (oven)

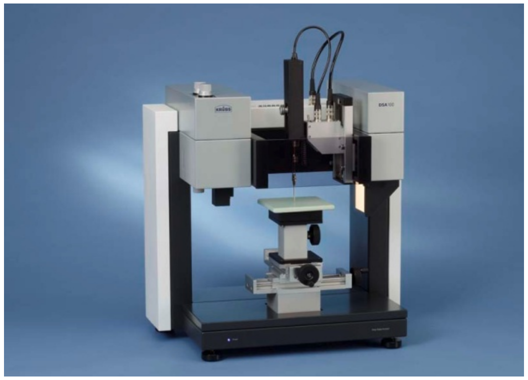
*Conventional

- Rosin adsorption on fiber
  - Fourier Transform Infrared Spectroscopy (FT-IR)
  - Field Emission Scanning Electron Microscope (FE-SEM)

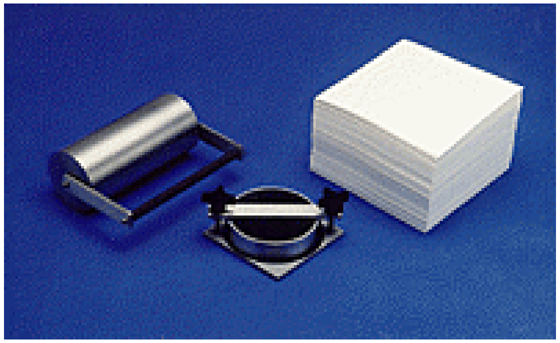
FT-IR, Nicolet 6700

FE-SEM, SUPRA 55VP

- Evaluation of hydrophobicity of paper sheet
  - Contact angle (30 sec)
    - TAPPI Test Methods T 558 om-97
  - Cobb sizing degree (900 sec)
    - TAPPI Test Methods T 411 om-98
    - *Weight of water, g/m²* = $\frac{final\ weight(g) - conditioned\ weight(g)}{Contact\ area(m^2)}$



Contact angle, DSA



Cobb sizing test

- Evaluation of physical properties of sheet
  - Formation: TechPAP formation tester
  - Bulk: T 411 om-97, L&W Micrometer
  - Roughness: T 555 pm-94, L&W PPS tester
  - Tensile strength: T 494 om-96, L&W tensile tester
  - Tear strength: T 414 om-98, L&W tear tester

Formation tester

Micrometer

PPS tester

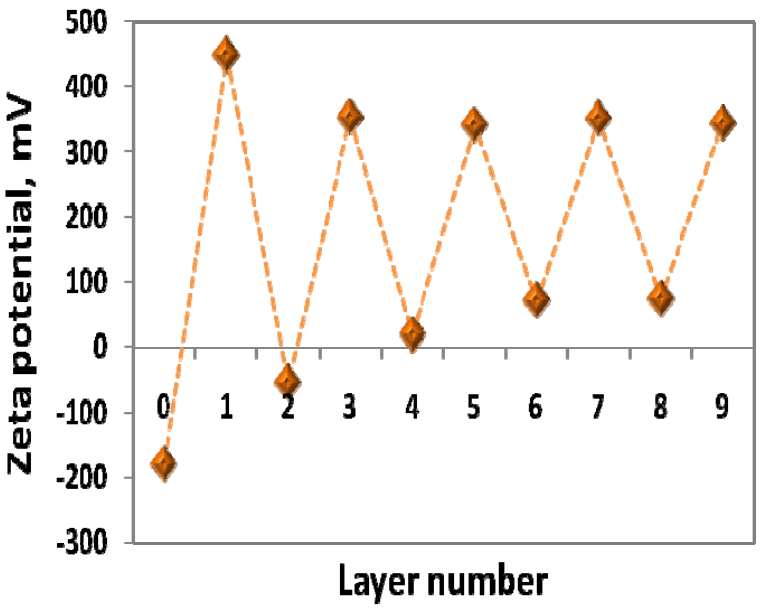
Tensile strength tester

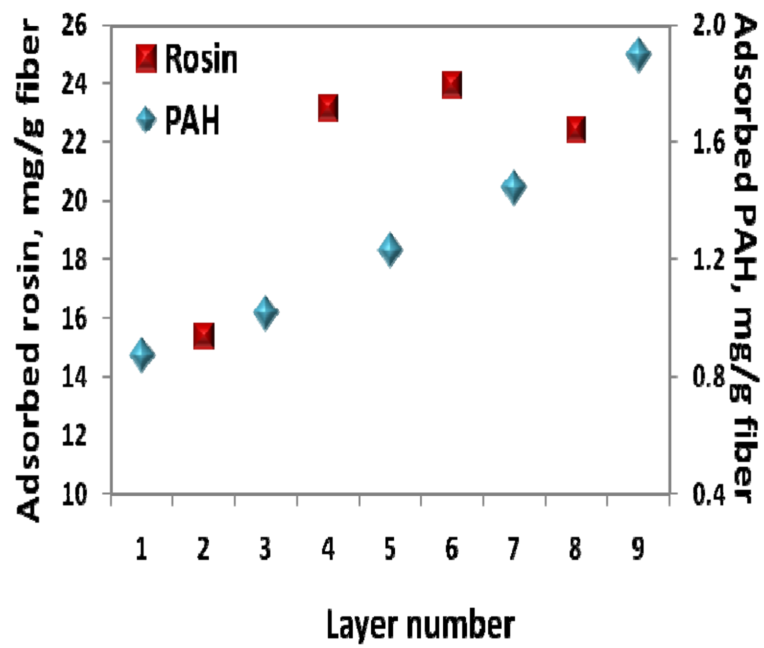
Tear strength tester

III. RESULTS

Electrochemical properties of fiber

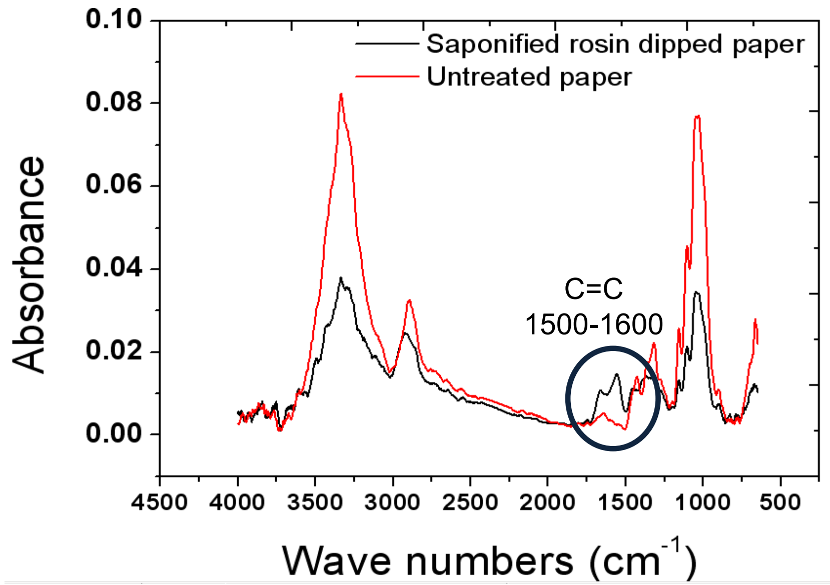
Cationic	PAH	+ 10.72 @ pH 7 + 7.34 @ pH 10
Anionic	Saponified rosin	- 0.26

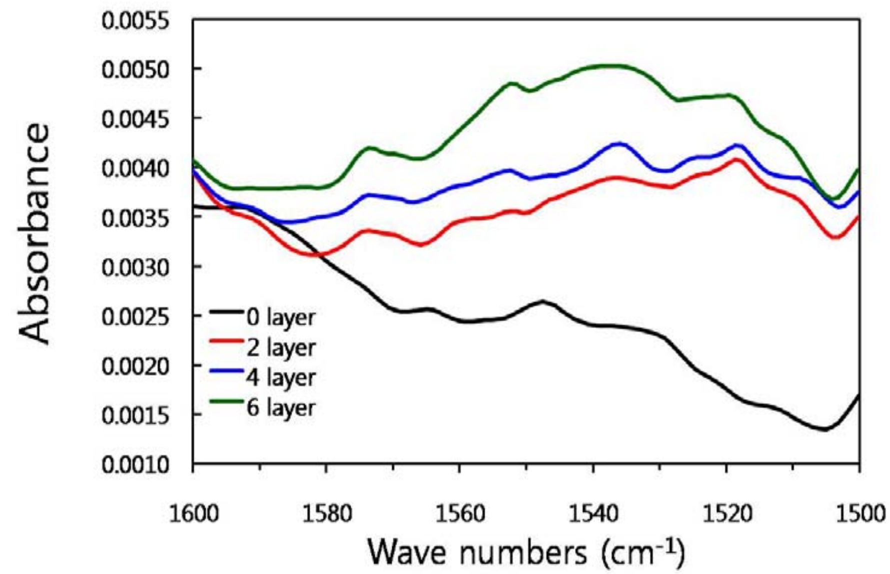




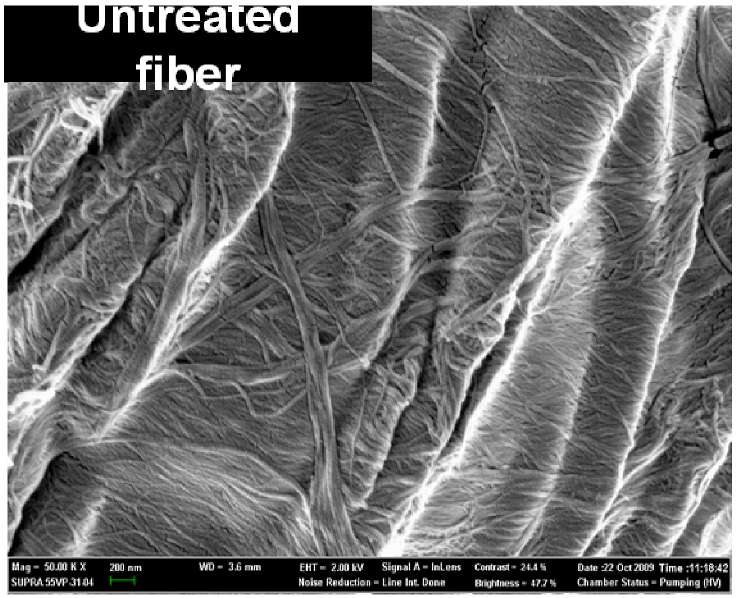
Adsorption of rosin on fiber

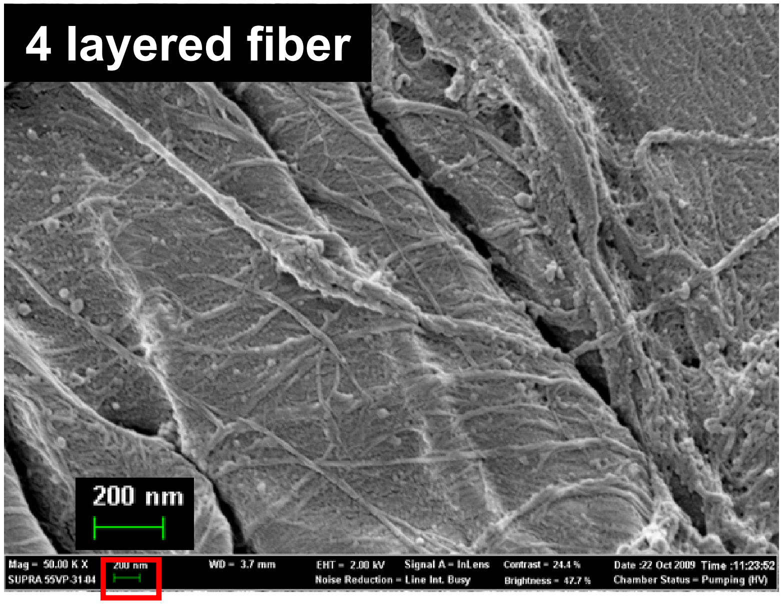
- FT-IR spectra

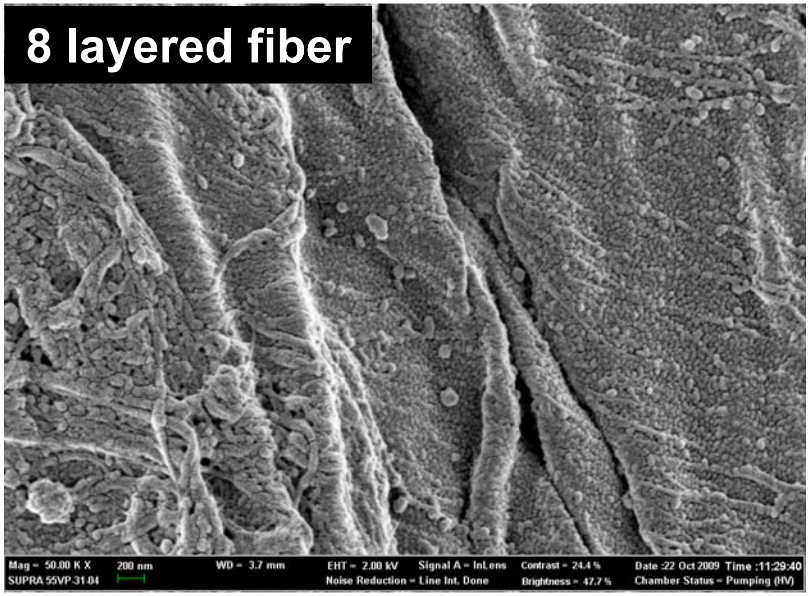




Adsorption of rosin on fiber





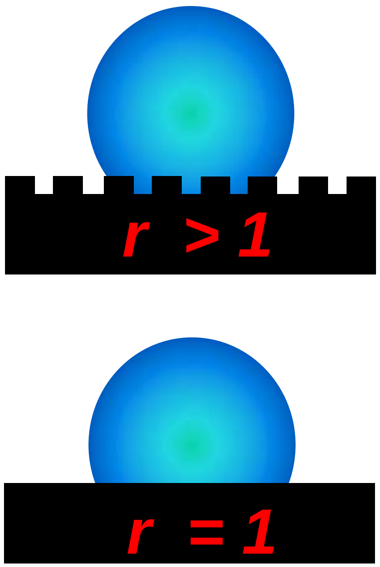


Hydrophobicity_Contact angle

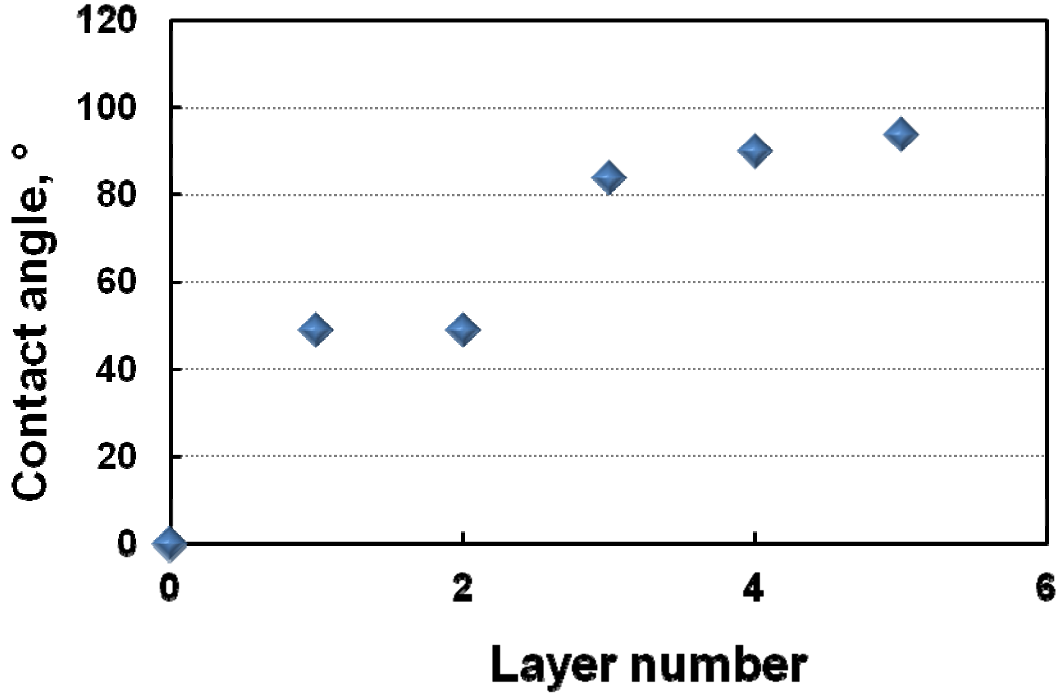
- Contact angle
  - Θ≥ 90˚ : hydrophobic
  - Wenzel equation

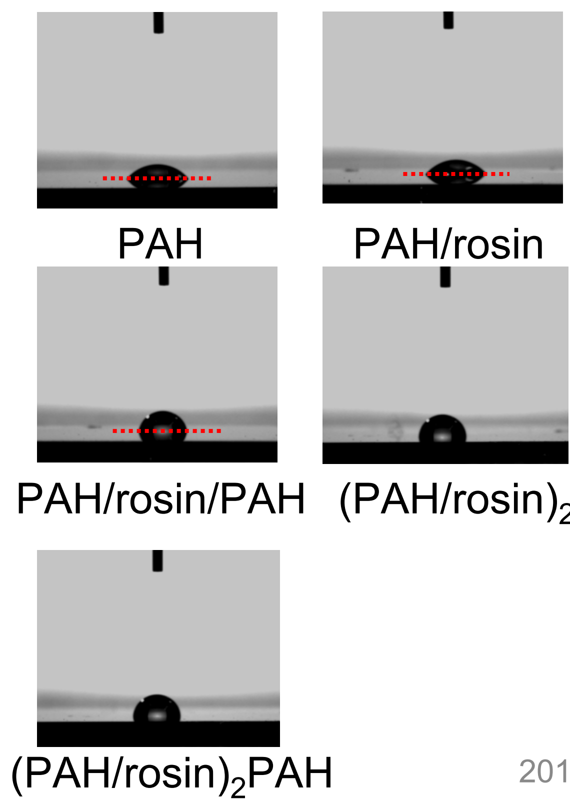
$$\cos \theta^* = r \cos \theta$$

θ^* = contact angle of the rough surface
θ = contact angle of flat surface
r = the ratio between the actual surface area of a rough surface to the projected one



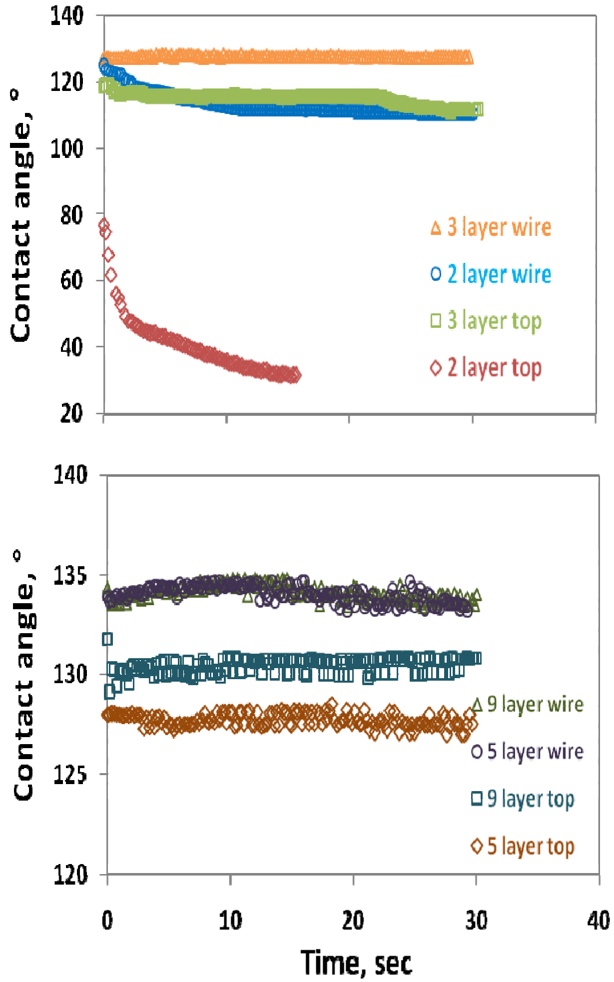
- Hydrophobicity of PAH and rosin layer
  - Successive spin coating of PAH and rosin on silicon wafer and drying at 50°C
  - Evaluation of contact angle

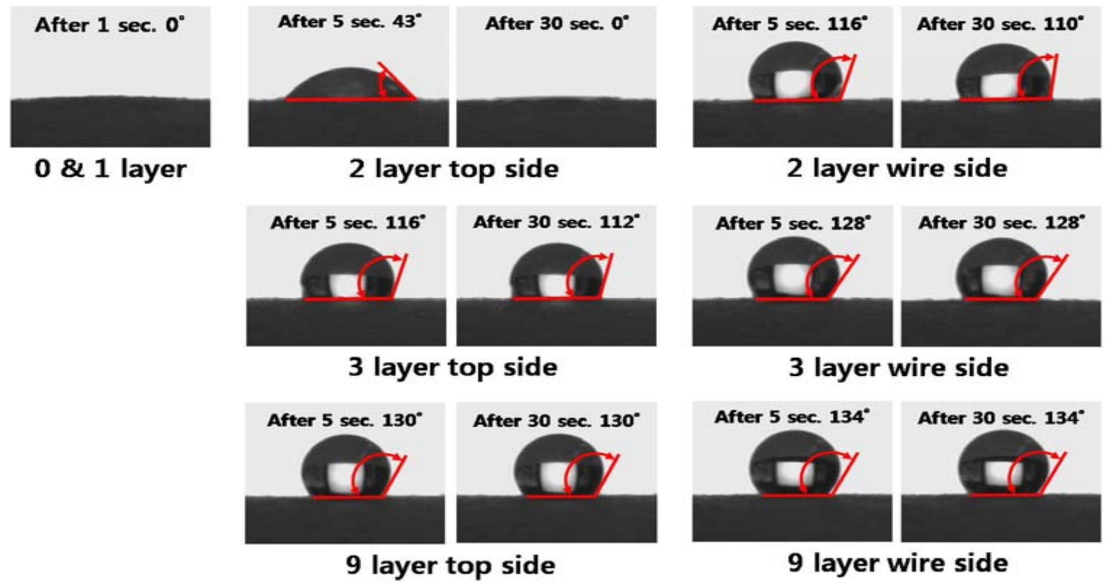




Hydrophobicity_Contact angle

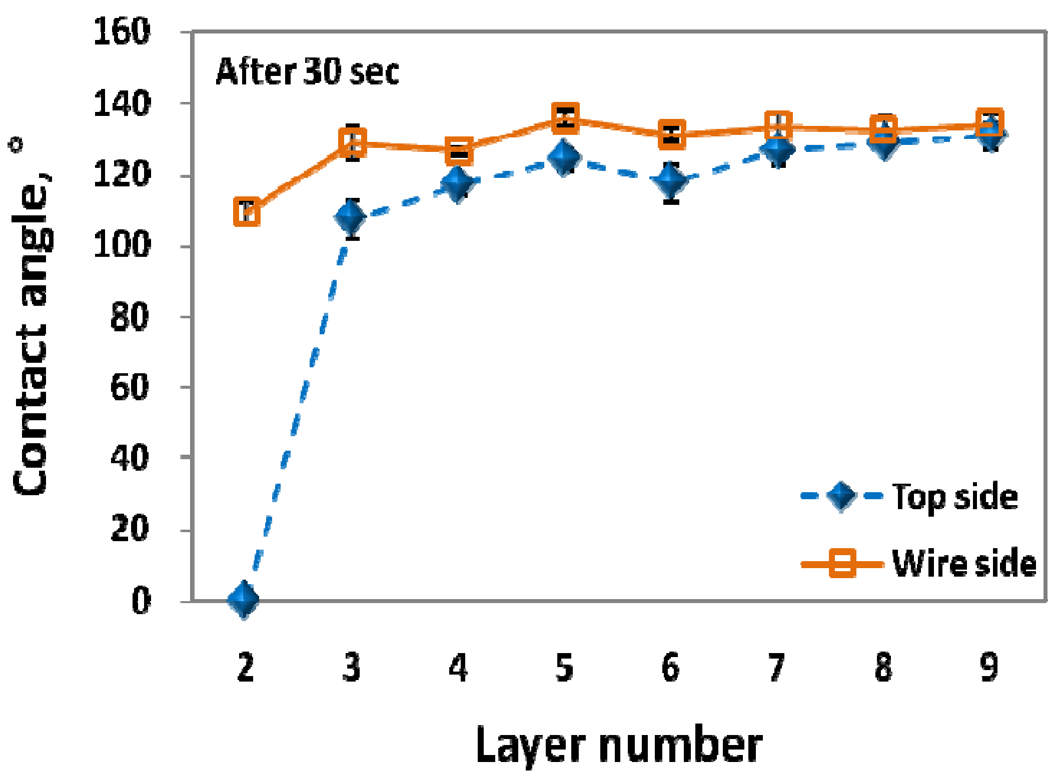
- Change of contact angle during 30 sec



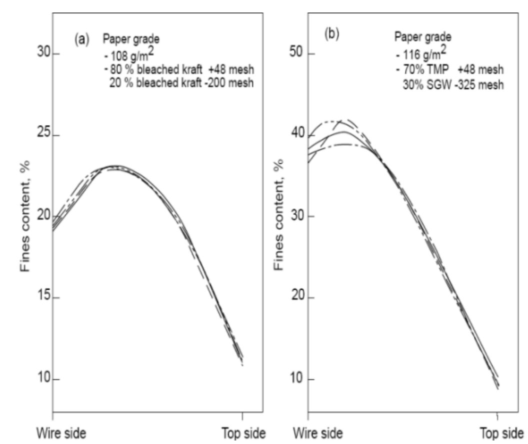


Hydrophobicity_Contact angle

- Contact angle at 30 sec after wetting

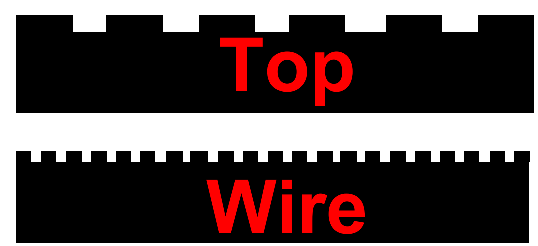


Z-D fines distribution

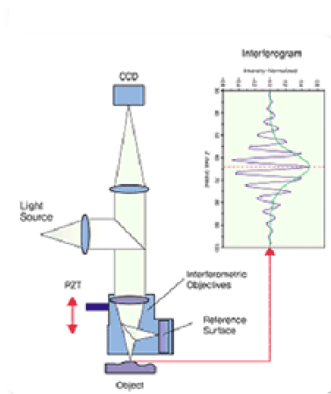


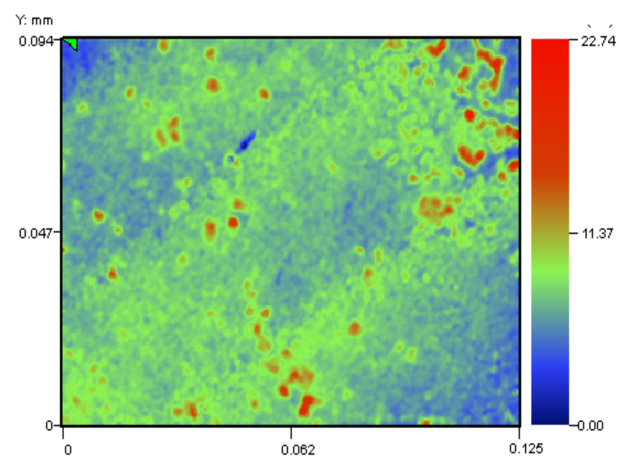
wire > top

(Z.Szikla and H.Paulapuro, Paperi Puu, 1986)

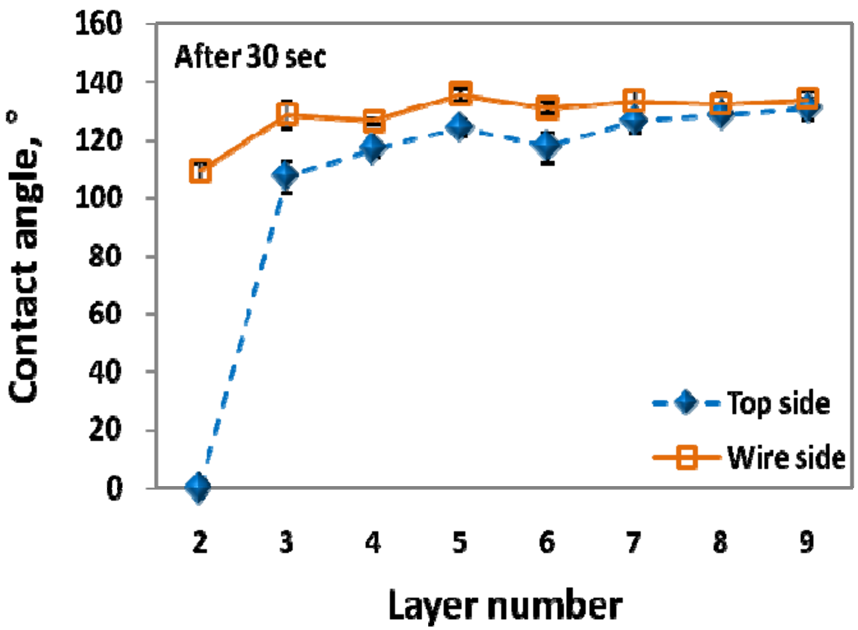


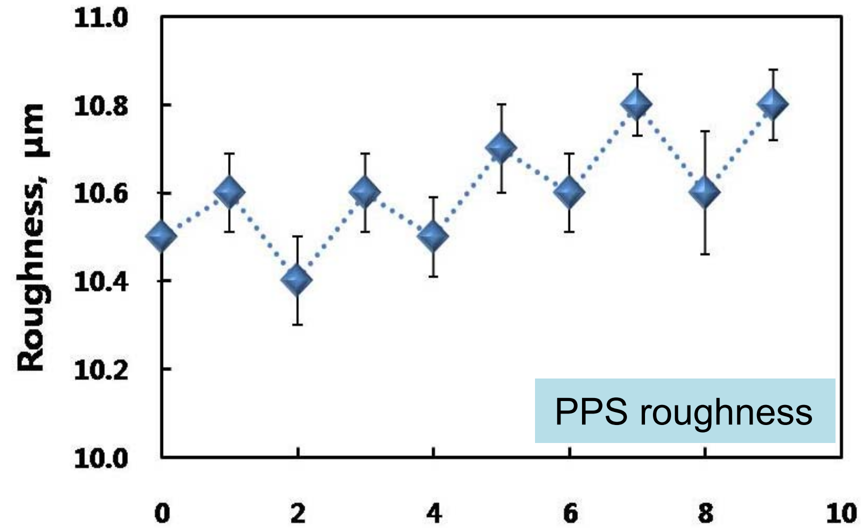
- Effect of roughness on contact angle
  - Wenzel model: $\cos\,\theta^* = r\,\cos\,\theta$
  - Measurement of roughness
    - PPS roughness of paper sheet : microscale
    - WLSI(white light scanning inteferometer) roughness of multilayered slide glass: nanoscale

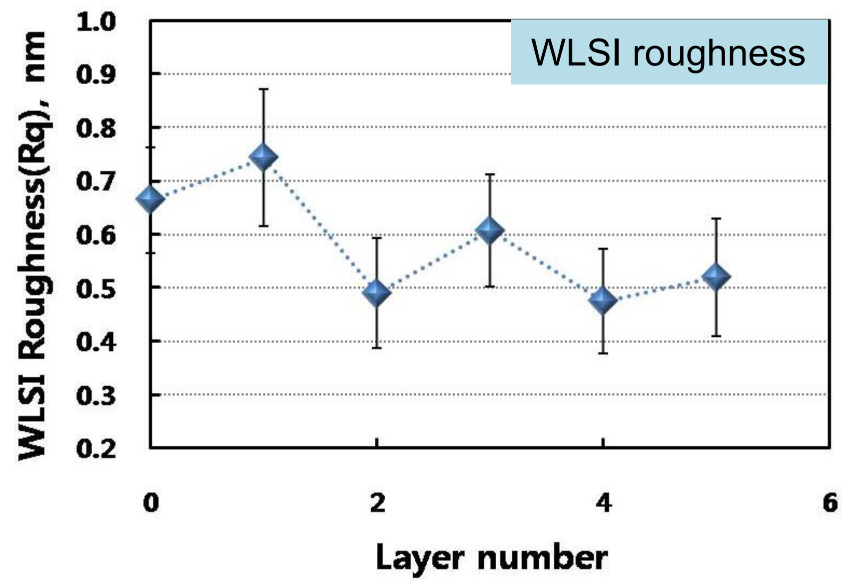


- Contact angle vs. Roughness

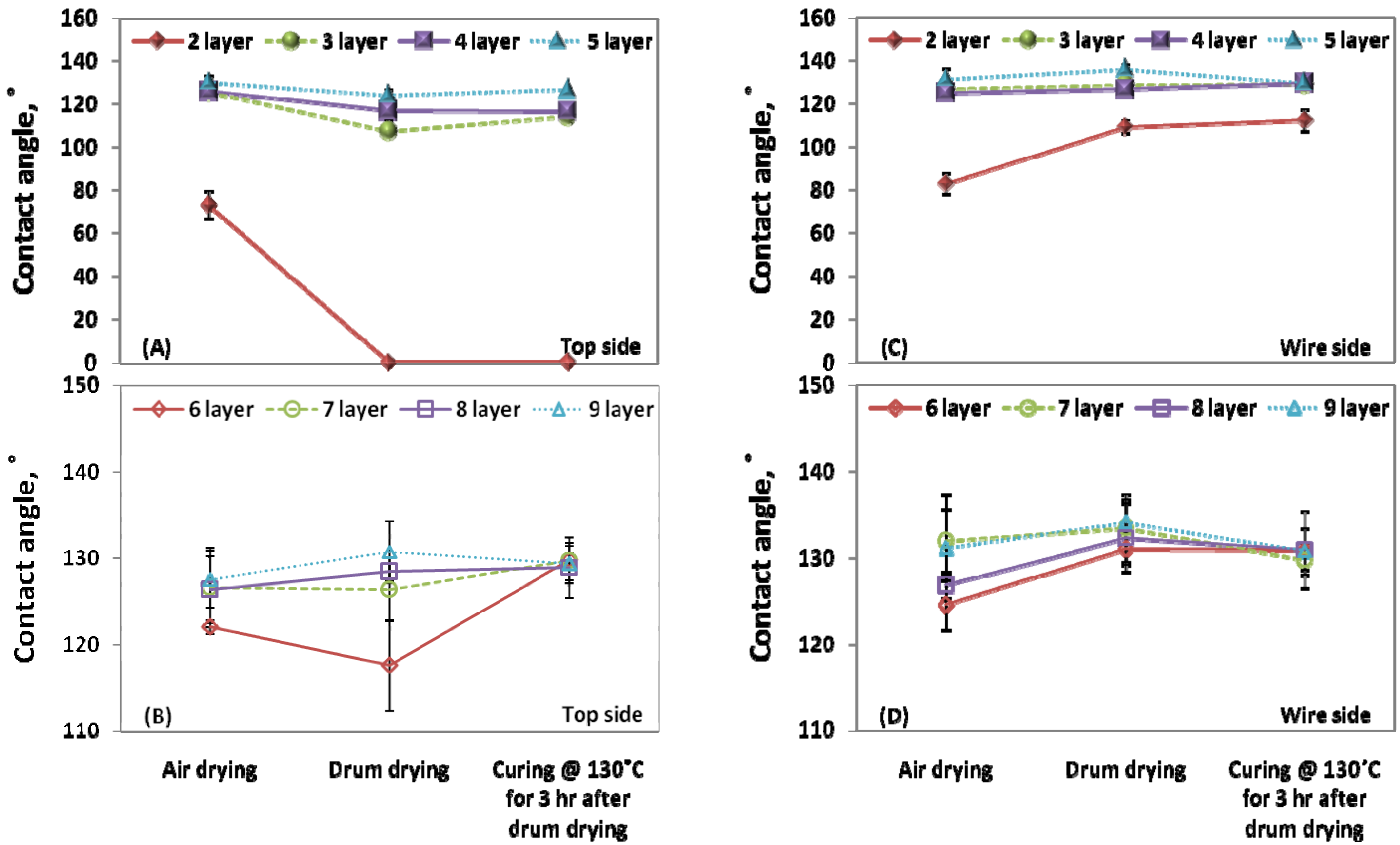




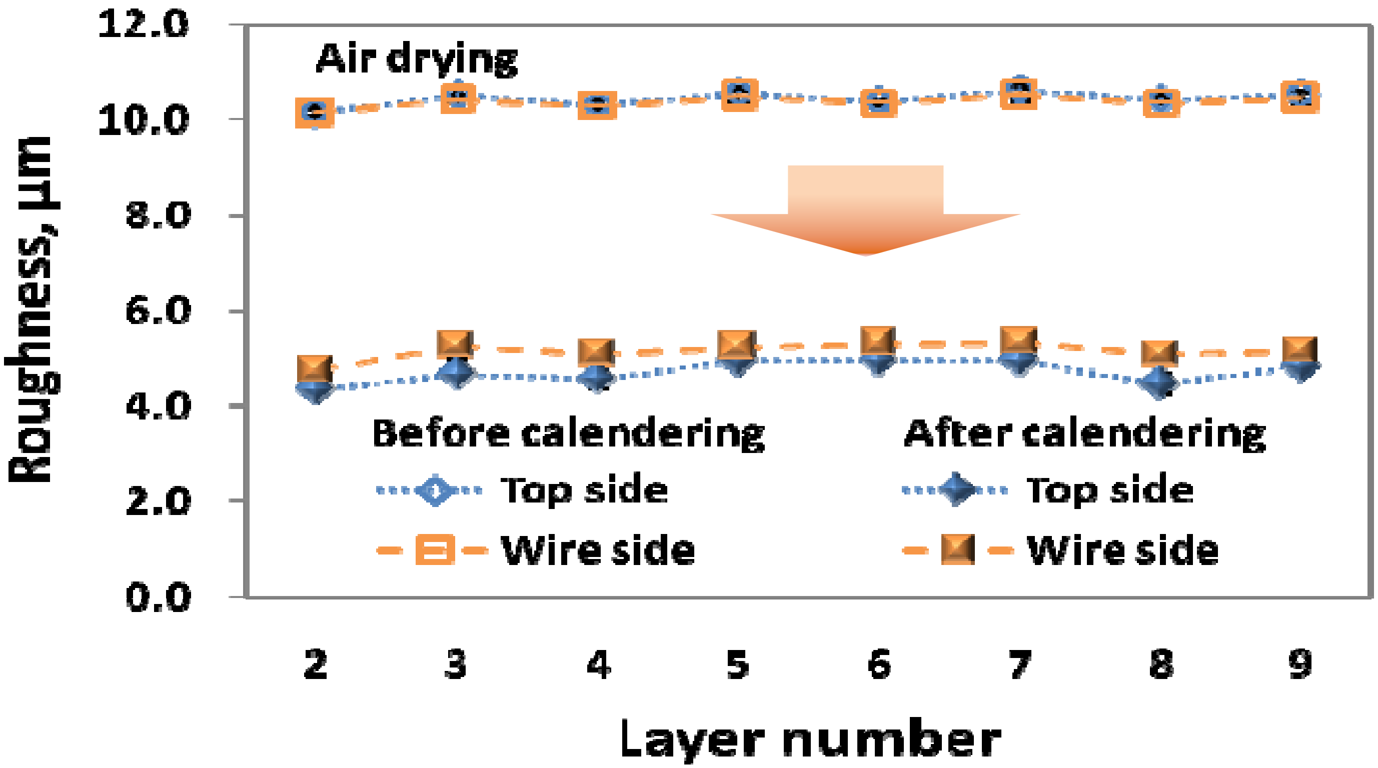


Hydrophobicity_Contact angle

- Effect of drying condition



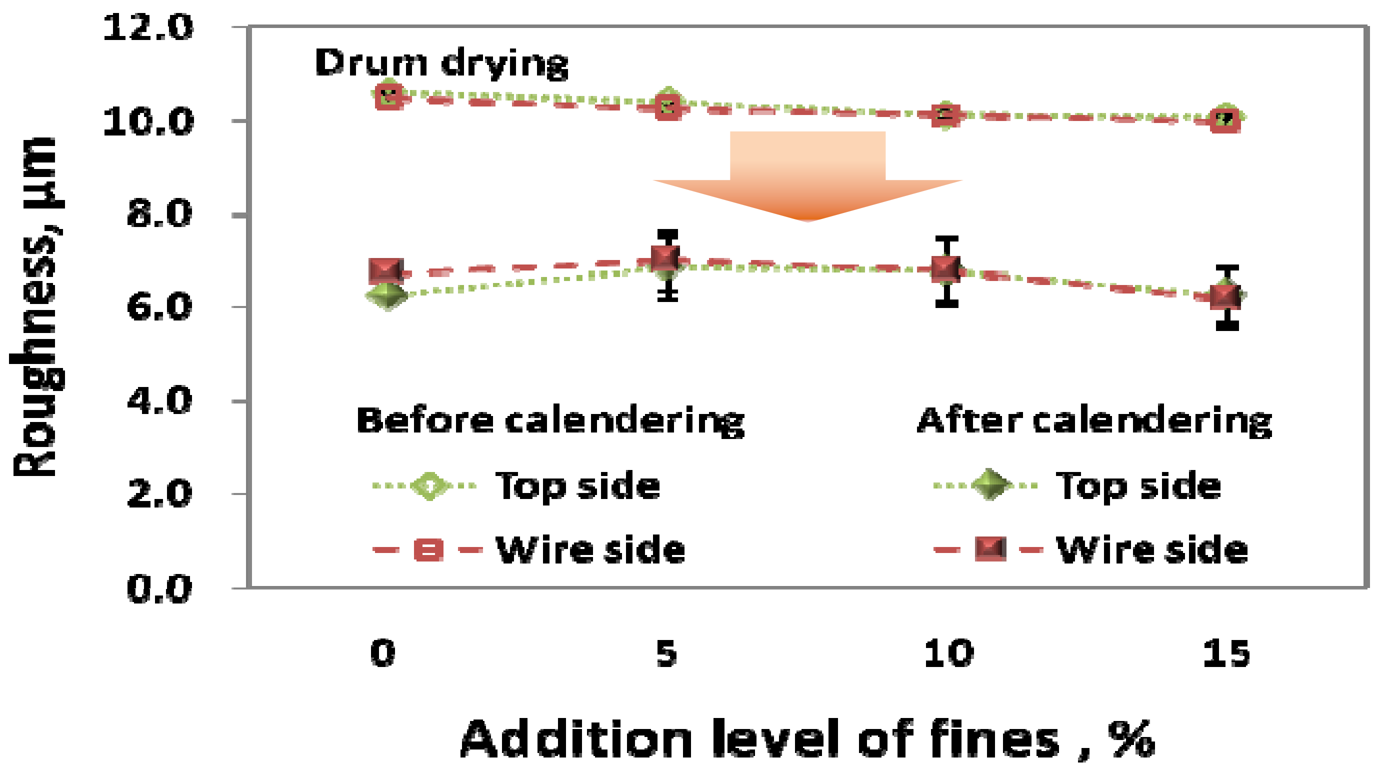
- Effect of calendering on PPS roughness



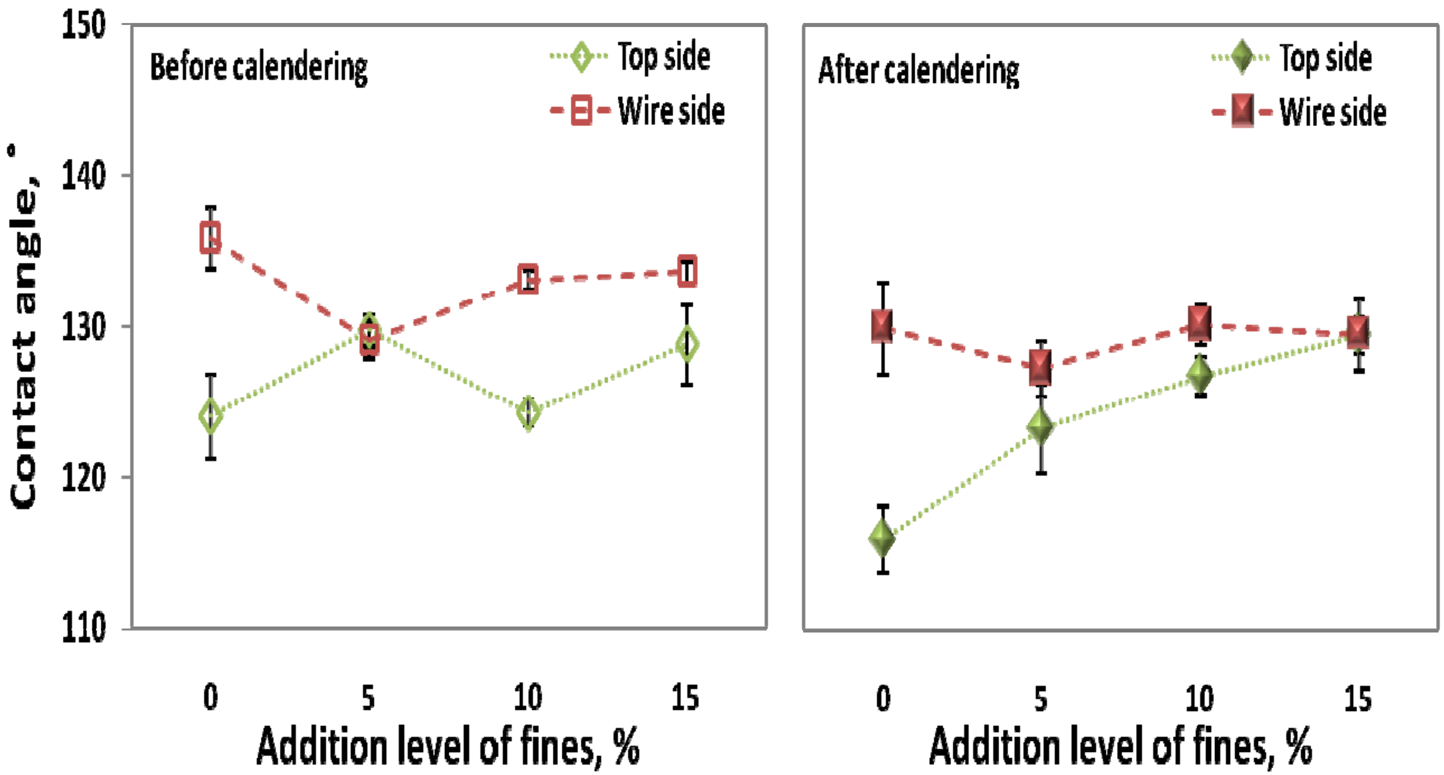
- Effect of calendering on contact angle

Layer No.	Contact angle, °					
	Top side			Wire side		
	Before	After	difference	Before	After	difference
2	73±6	11±2	62	83±5	8±3	75
3	126±3	121±2	5	127±1	123±1	4
4	126±3	116±2	10	125±1	115±2	10
5	130±3	128±2	2	130±4	131±3	-1
6	122±1	115±3	7	125±2	120±2	5
7	127±5	129±3	-2	132±4	129±1	3
8	125±3	119±3	6	127±1	119±1	8
9	128±3	124±2	4	128±1	128±3	0

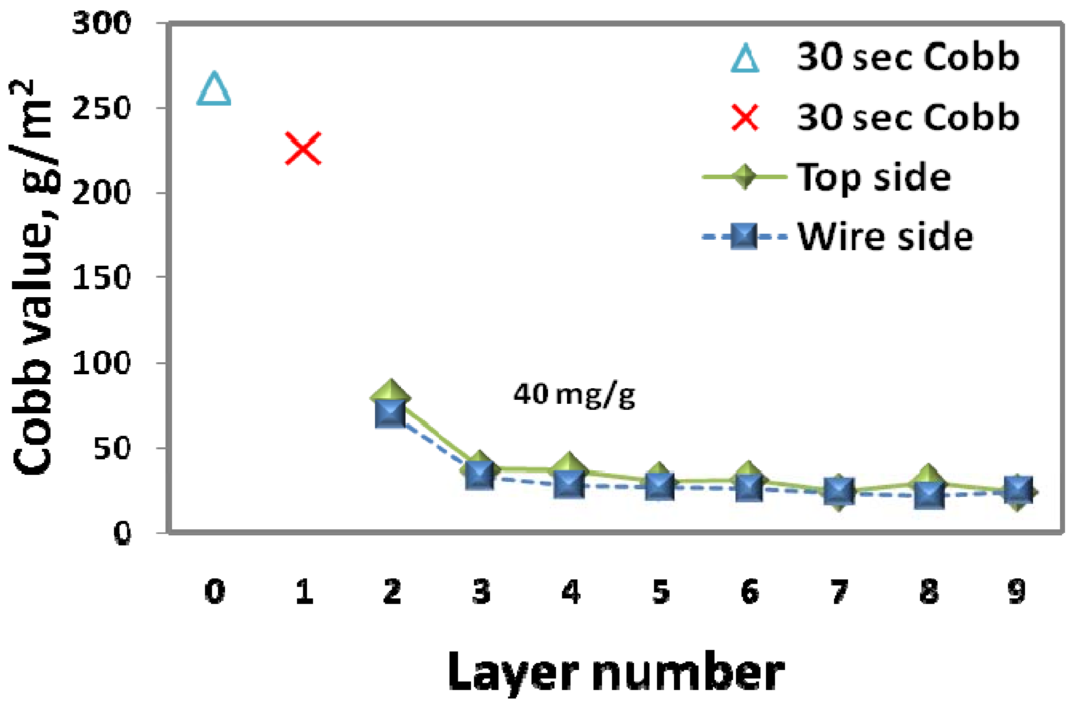
- Effect of fines addition on roughness(@ 5 layer)



- Effect of fines addition on contact angle (@ 5 layer)

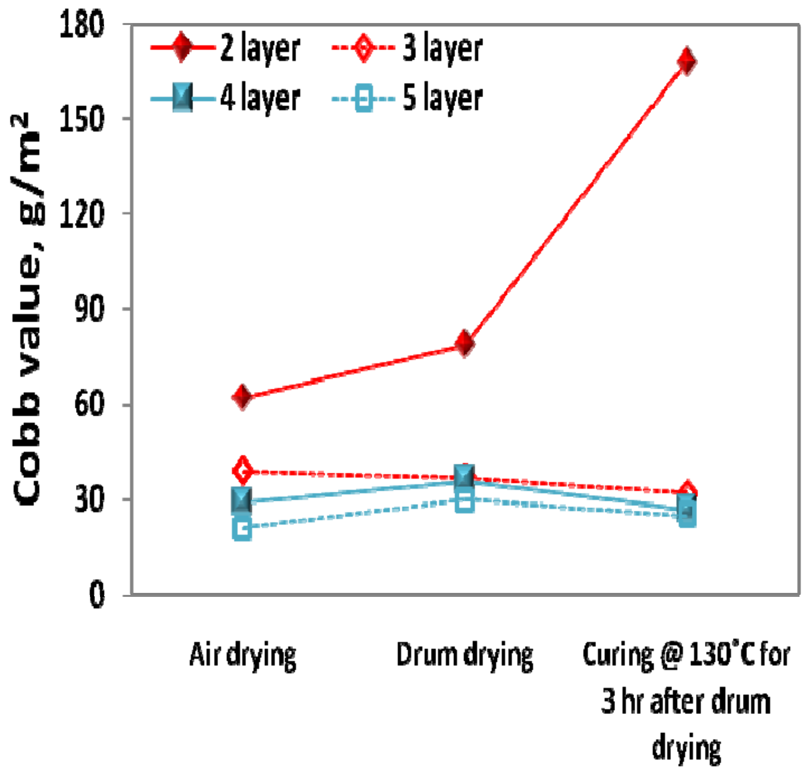


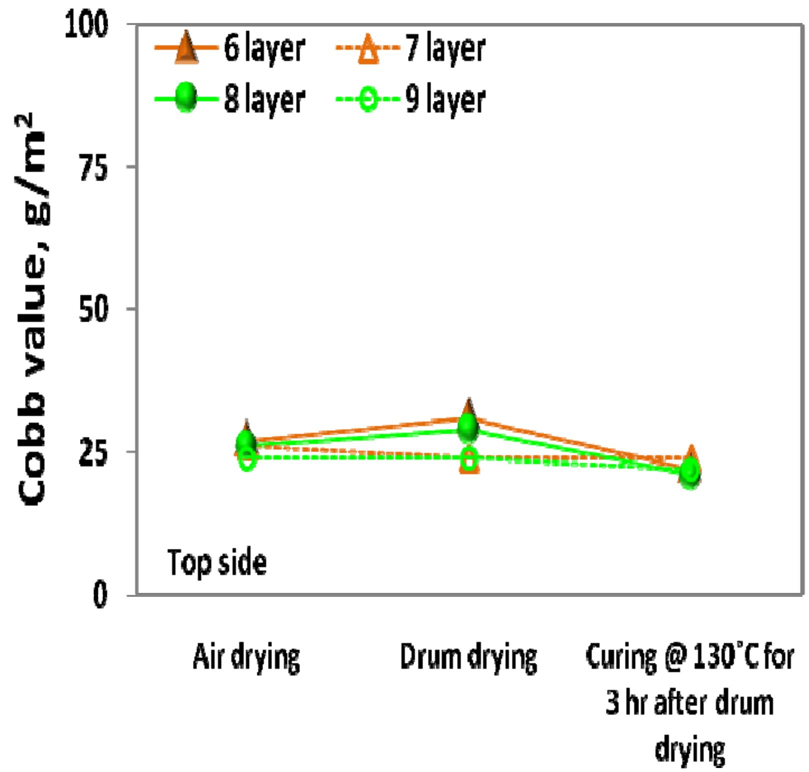
Hydrophobicity_Cobb sizing degree



Hydrophobicity_Cobb sizing degree

- Effect of drying condition





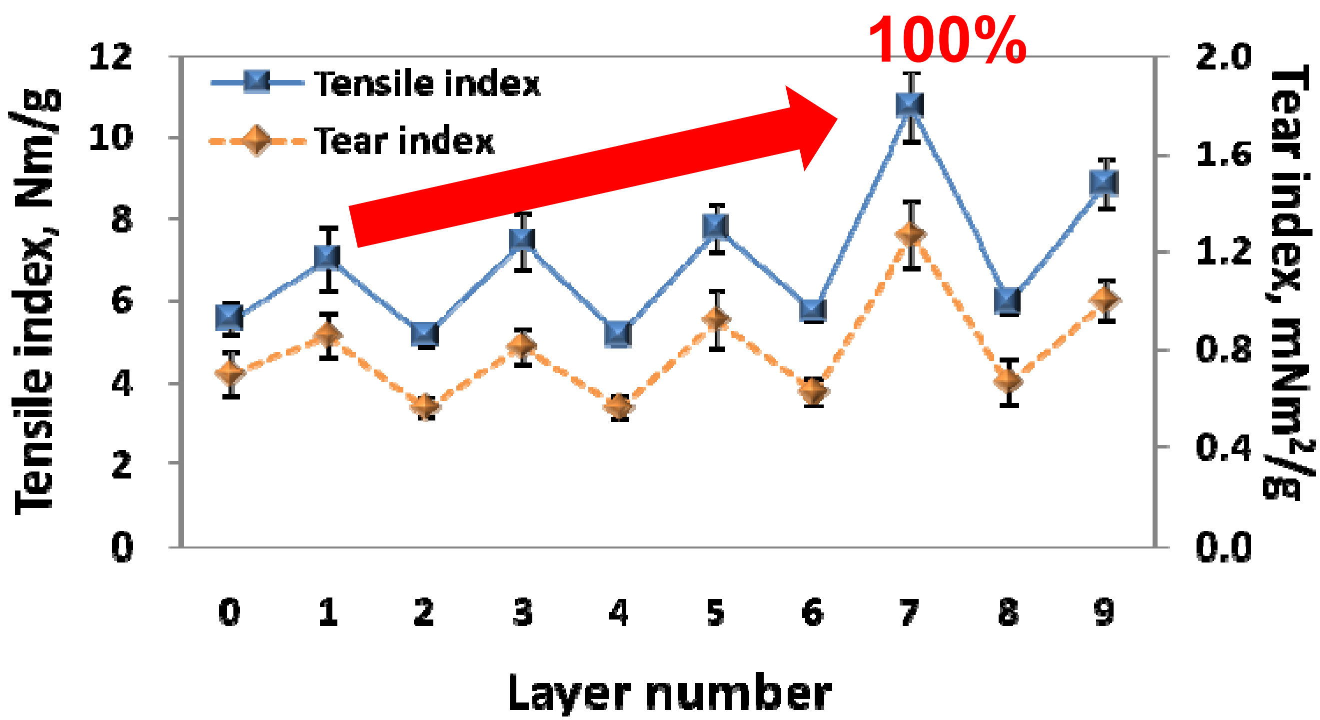
Physical properties of sheet

- Effect of layer number

	Layer number									
	0	1	2	3	4	5	6	7	8	9
Formation (L_T)	42±2	44±3	48±6	43±3	48±6	46±2	44±3	46±2	46±2	49±3
Bulk (cm^3/g)	2.82 ±0.05	2.79 ±0.06	2.82 ±0.03	2.78 ±0.03	2.82 ±0.03	2.79 ±0.04	2.82 ±0.03	2.80 ±0.04	2.80 ±0.03	2.86 ±0.07

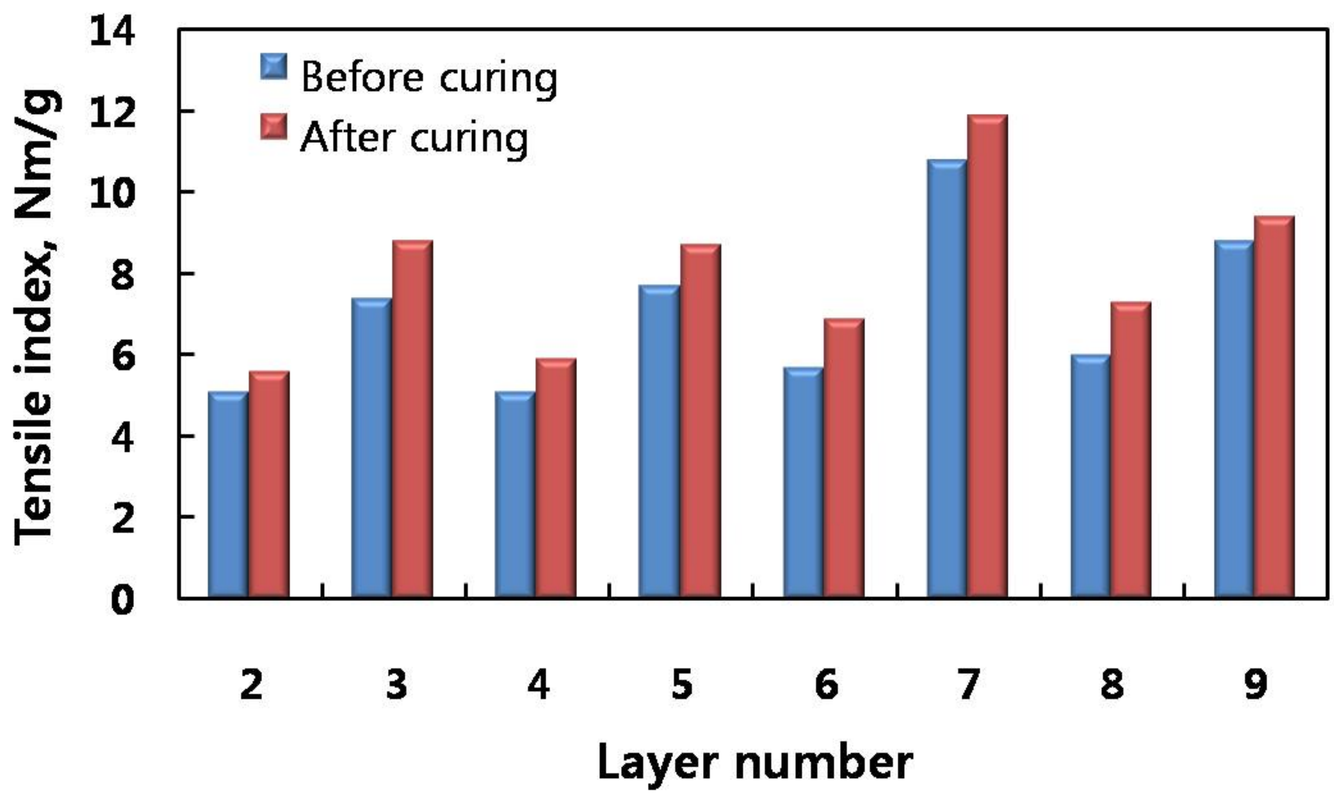
Physical properties of sheet

- Effect of layer number



Physical properties of sheet

- Effect of curing on tensile strength



IV. CONCLUSIONS

Conclusions

- **The adsorption of rosin on pulp fiber was confirmed by and FT-IR and FE-SEM.**
- **Paper sheet with strong hydrophobicity and water resistance could be made using pulp fibers with at least 4 layers of PAH and rosin.**
- **Nan- and micro-scale roughness caused by mulitlayering and fines presence had a positive effect on the increase of contact angle, but it is not enough to show superhydrophobicity.**
- **When pulp fiber had PAH in the most outer layer, the tensile and tear strengths of paper sheet were increased .**
- **PAH layer contributed to paper hydrophobicity with proper orientation and anchoring of rosin by electrostatic force and nanoscale roughness by morphology, and paper strength by improved conformability.**

Acknowledgement

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Thank you for your attention.