Dielectric-Barrier Discharge Fiber Modification Wet Strength Improvements

Institute of Paper Science and Technology

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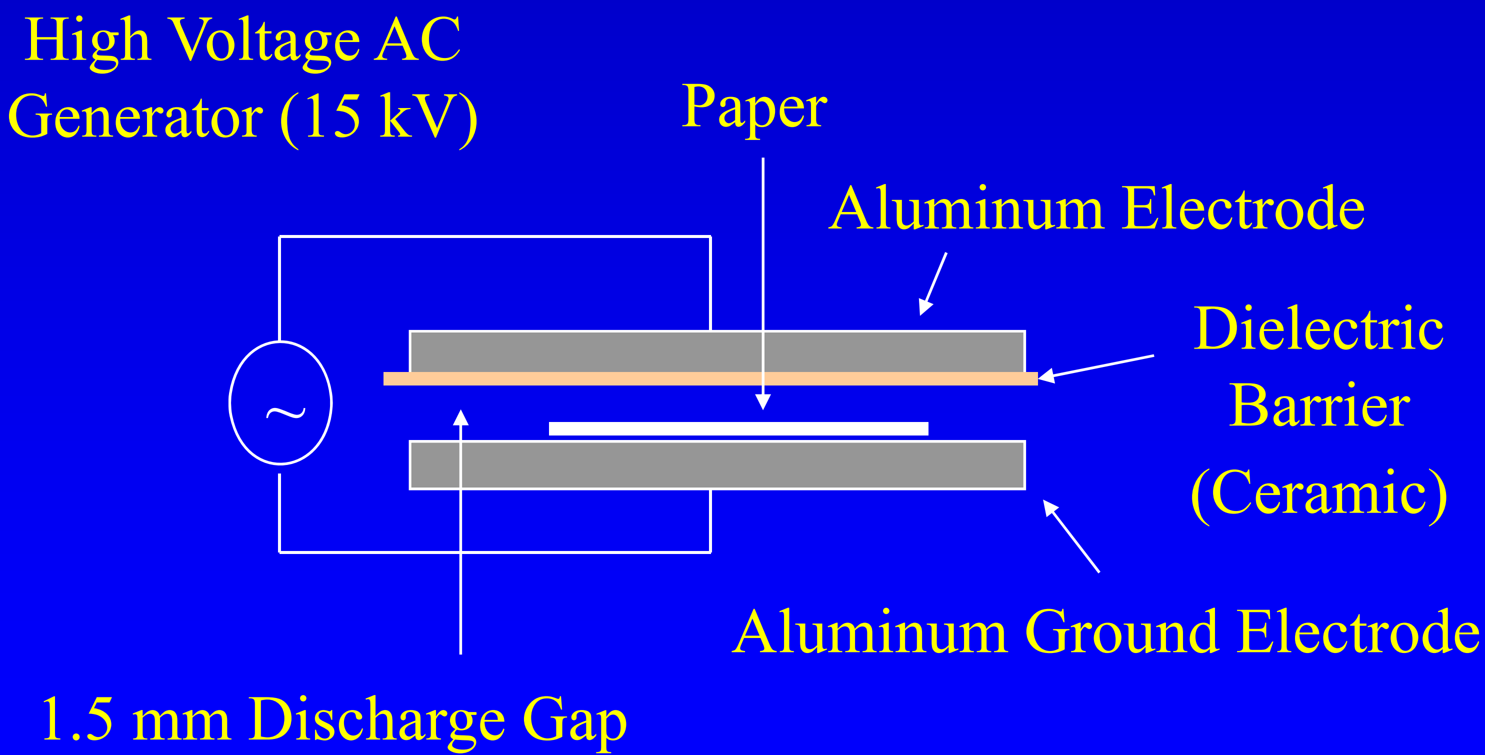
Hypotheses

- DBD-initiated chemistry will:
  - Enhance fiber surface topo-chemistry
- DBD-initiated modifications to fiber surface chemistry will:
  - Improve product performance

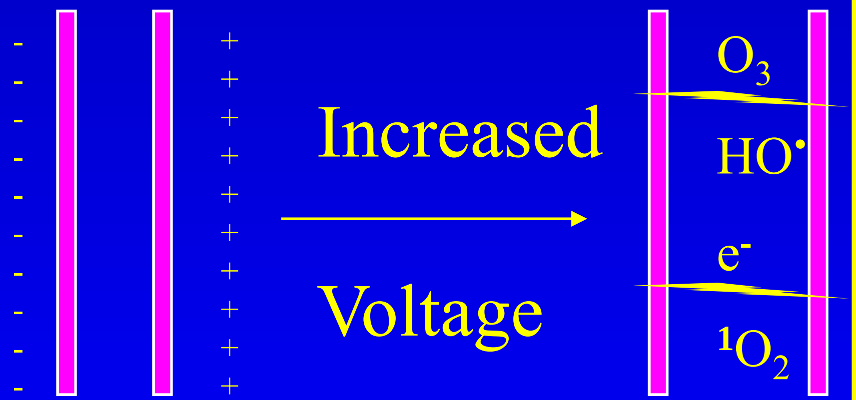
Objectives

- Investigate impacts on product performance
- Characterize impacts to fiber surface topo-chemistry
- Explain mechanisms by which changes in physical properties occur

Dielectric-Barrier Discharge



DBD



Plasmas: Surface oxidation/grafting of polymeric films and cellulosics via free radical reactions at atmospheric conditions

Goring (1967), Brown & Swanson (1971) at IPC, Back & Danielsson (1987/1988) at STFI, Sapieha with Bataille, Belgacem & others at Ecole Polytechnic (1990s), Kemppi (1990s)

Raw Materials: Pulps

- Softwood BKP
  - Long Fiber Fractions
- Softwood Unbleached TMP
  - Long Fiber Fractions

Raw Materials: TMP & BKP

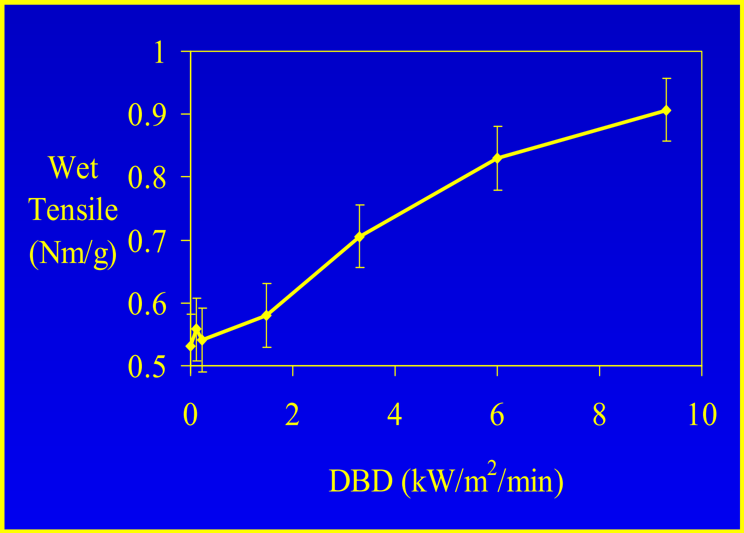
- TMP - Extraction 24 Hours*
- Form Sheets
- Condition Sheets
- Surface Treatment
- Extract for surface analysis*

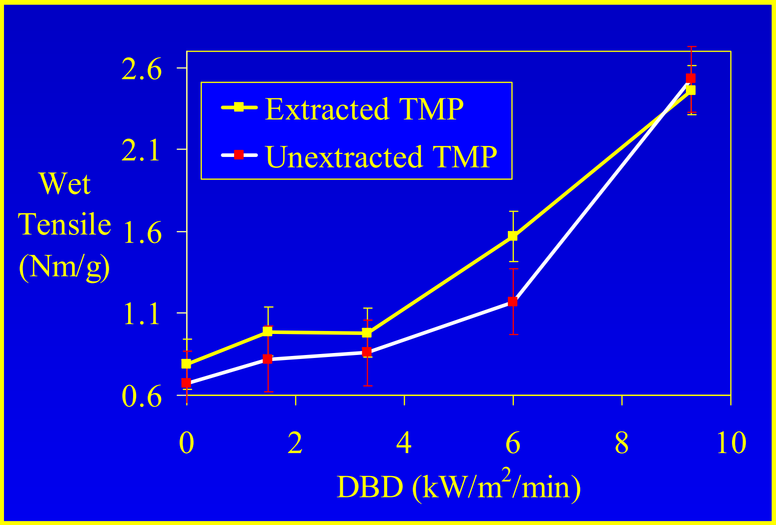
*As needed

Objectives

- Investigate impacts on product performance
- Characterize impacts to fiber surface topo-chemistry
- Explain mechanisms by which changes in physical properties occur

Wet Strength

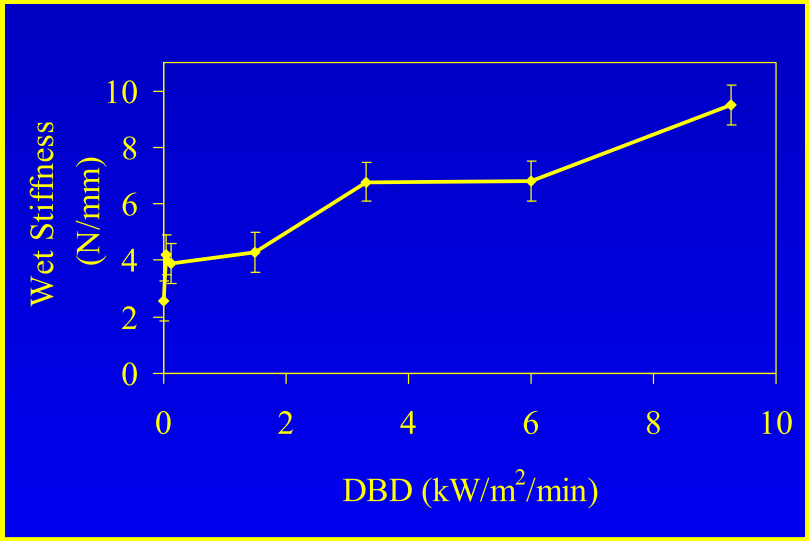


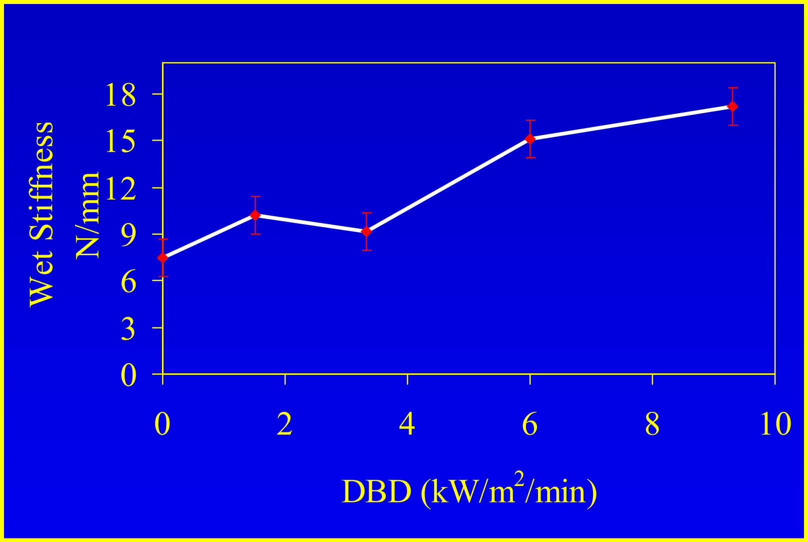


Increasing DBD treatment results in increased wet tensile index of BKP and TMP

Vander Wielen, L.C.; Page, D.H.; Ragauskas, A.J. Holzforschung, 2004

Wet Stiffening

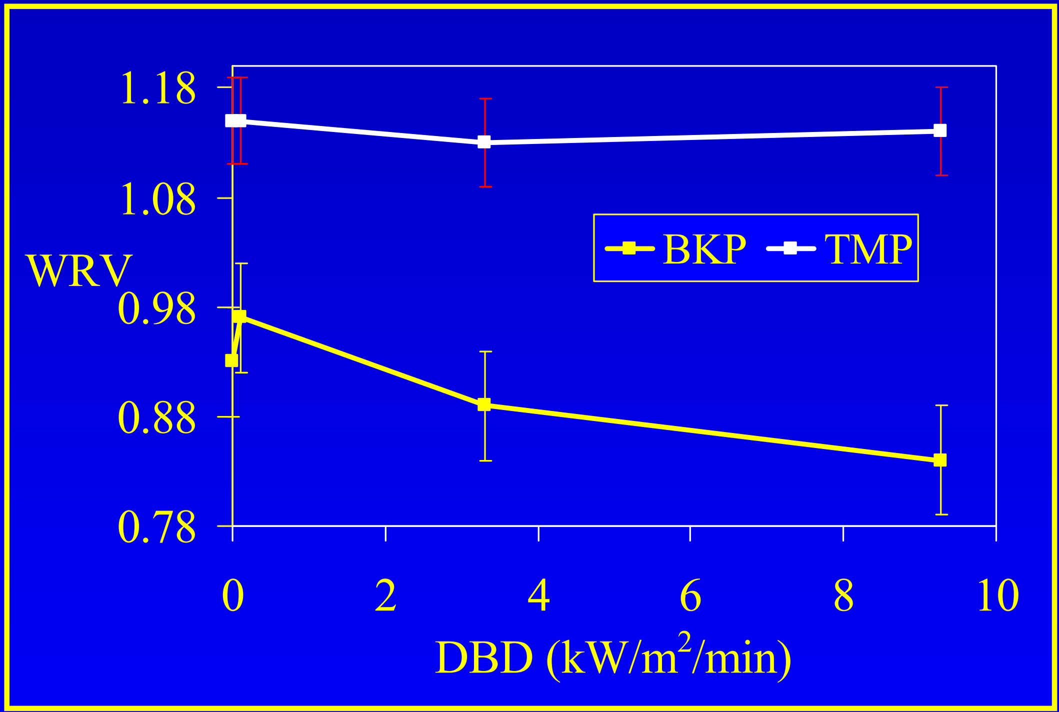




Wet stiffness of BKP and TMP increases with increased DBD treatment

Vander Wielen, L.C.; Ragauskas, A.J. Nordic Pulp & Paper Reseearch Journal, 2004

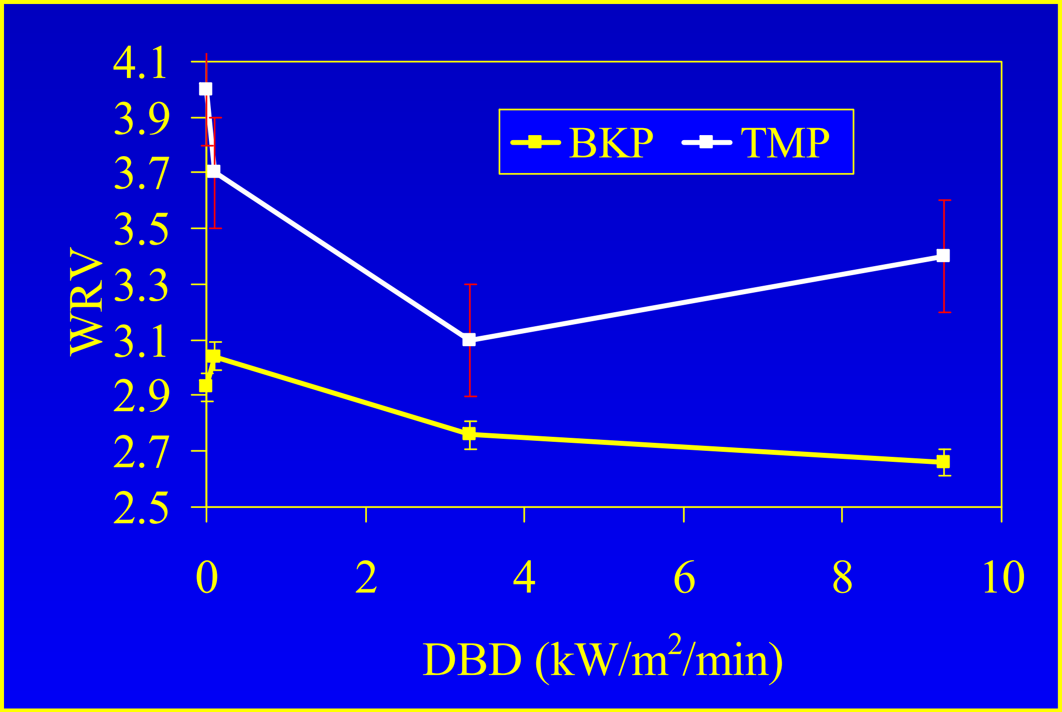
Fiber Swelling: Tappi 256



BKP fiber swelling initially increases, then decreases with increased DBD treatment

Vander Wielen, L.C.; Elder, T.; Ragauskas, A.J. Cellulose 2004

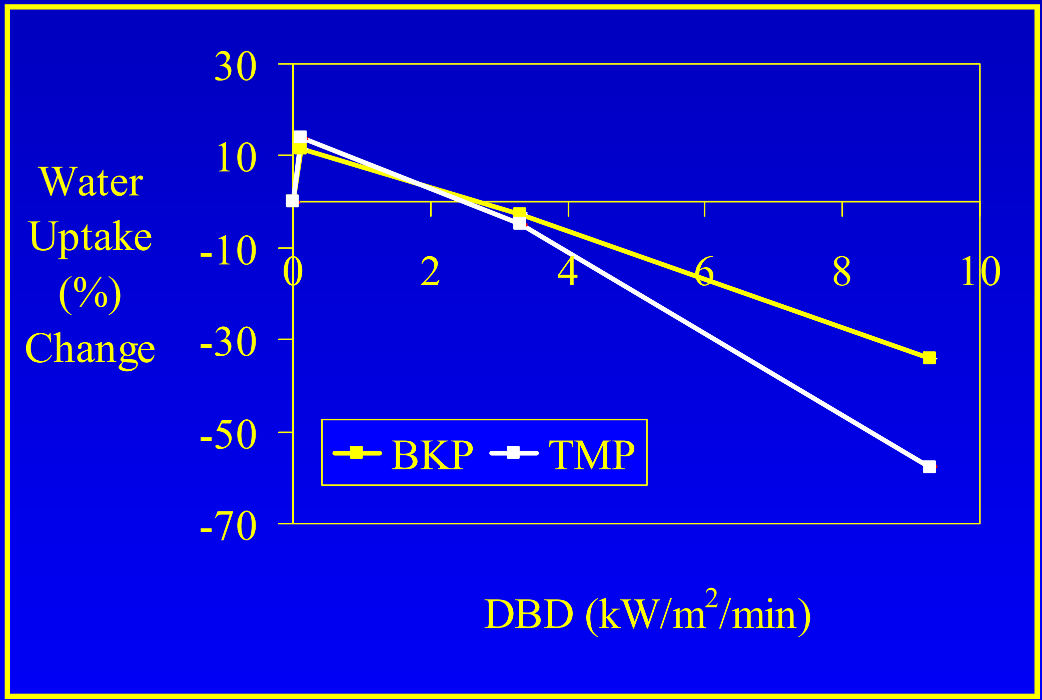
Fiber Swelling: Modified WRV



BKP fiber swelling initially increases, then decreases with increased DBD treatment

Vander Wielen, L.C.; Ragauskas, ACS Symposium Series, 2004

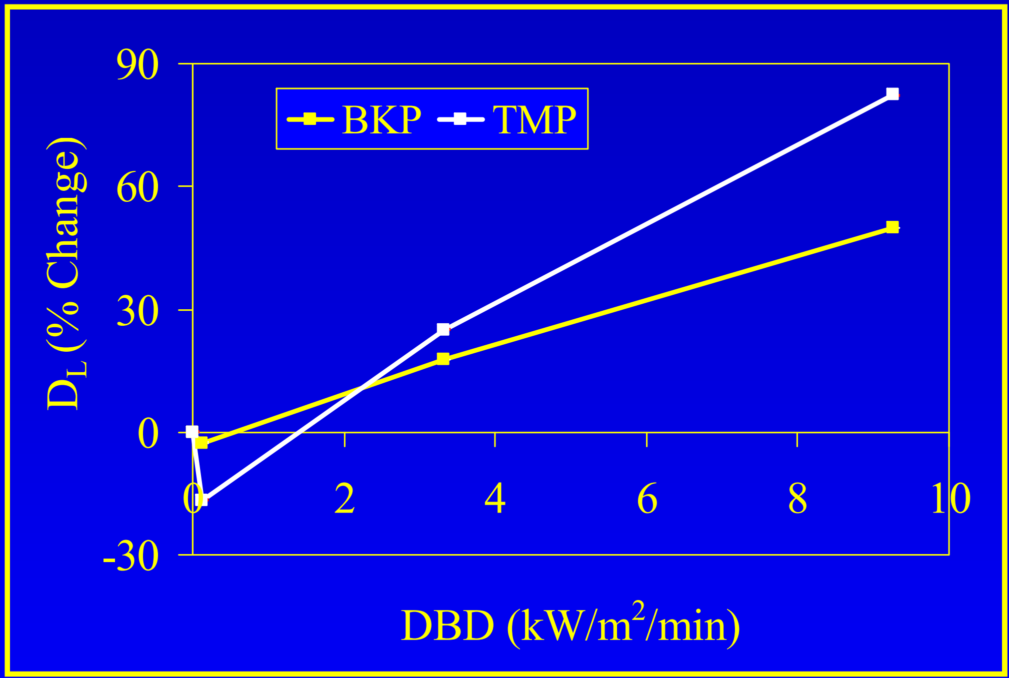
Water Uptake



Fiber % change in water uptake increases with low treatment, decreases with increased DBD treatment

Vander Wielen, L.C.; Page, D.H.; Ragauskas, A.J. Holzforschung, 2004

Linear Dimensional Stability



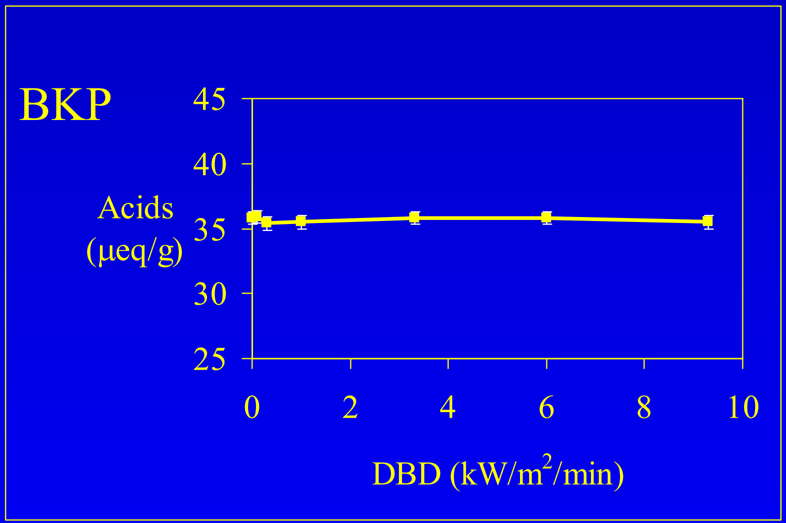
Linear dimensional stability decreases with low treatment, increases with increased DBD treatment

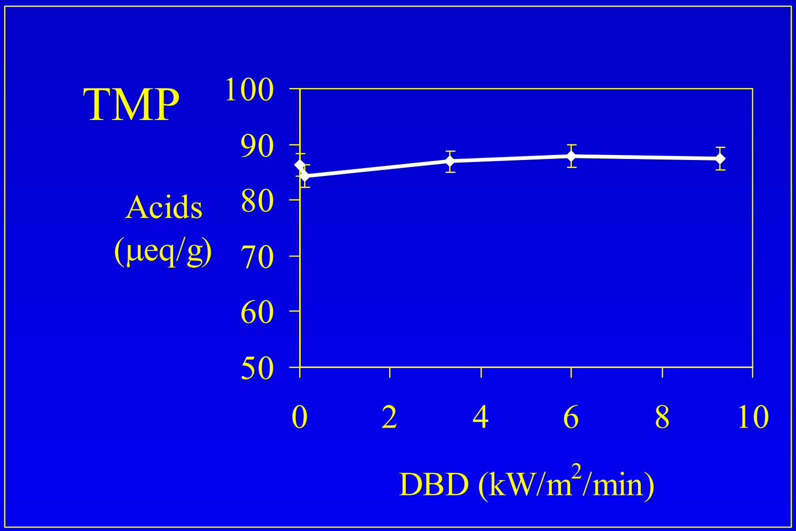
Vander Wielen, L.C.; Page, D.H.; Ragauskas, A.J. Holzforschung, 2004

Surface Analysis: DBD Treated Fibers

- Titration Methods
- DCA
- ESCA (XPS)
- AFM

Conductometric Titration

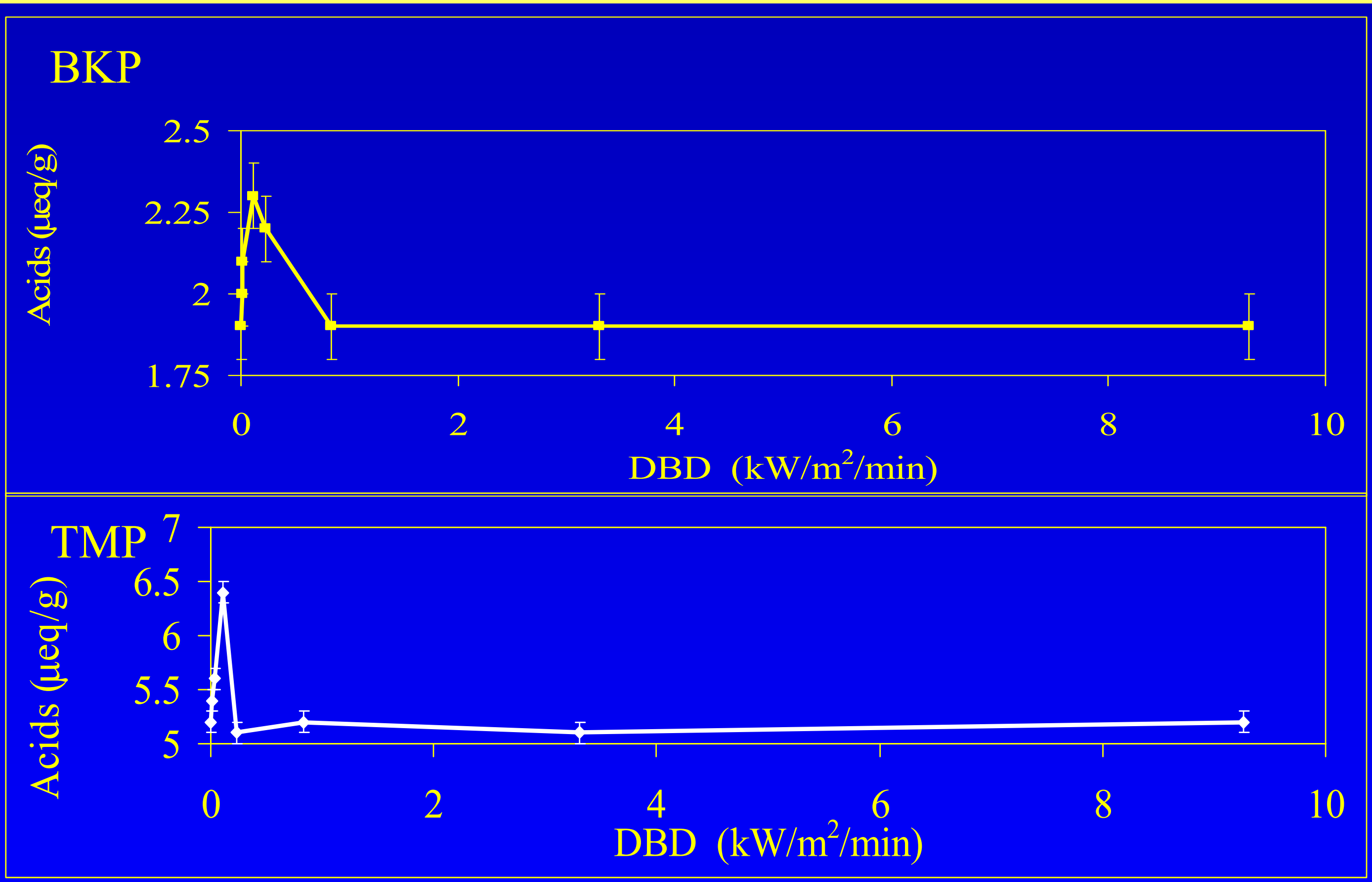




No change in BKP/TMP total acid groups seen with DBD treatment

Vander Wielen, L.C.; Ragauskas, A.J. 12th ISWPC Proceedings, Vol 1, p. 373, 2003

Polyelectrolyte Titration



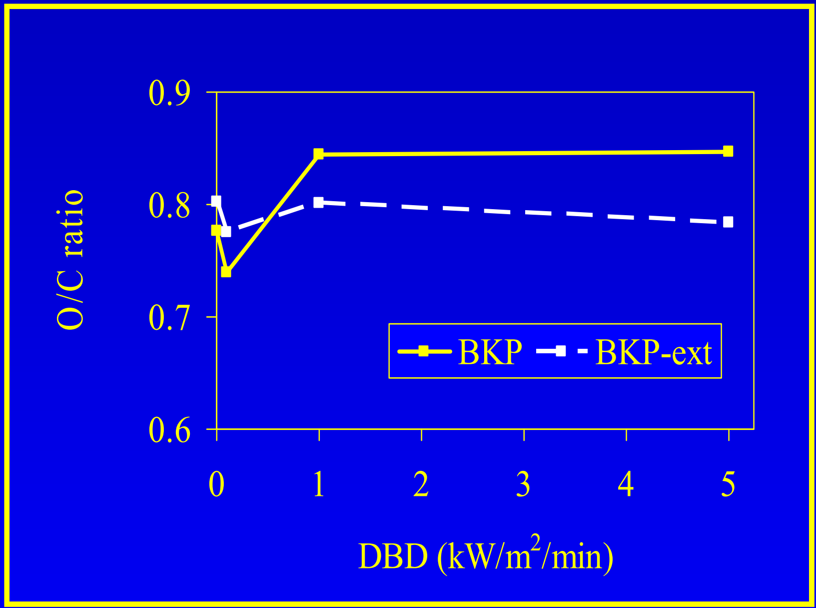
BKP/TMP surface acid groups initially increase, then decrease with increased DBD treatment

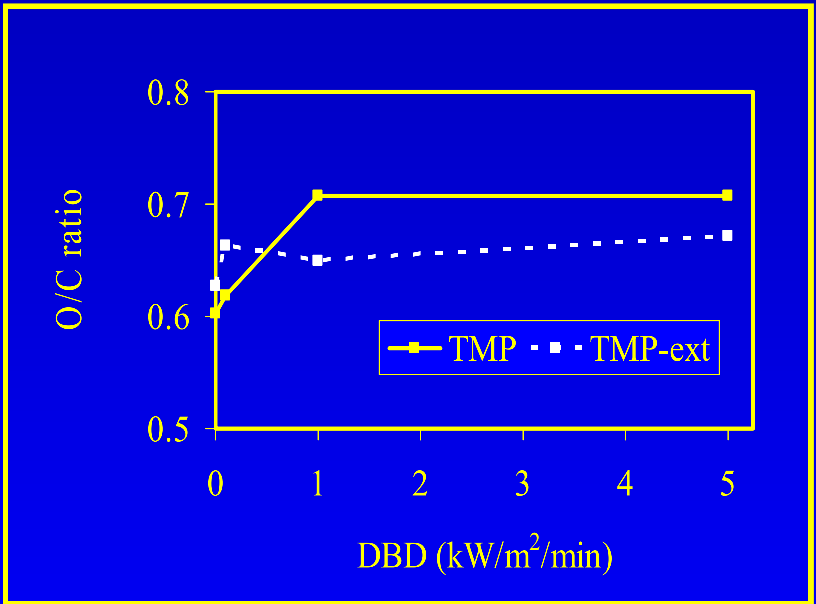
Vander Wielen, L.C.; Ragauskas, A.J. 12th ISWPC Proceedings, Vol 1 p. 373, 2003

Fiber Surface Analysis - ESCA

- Physical Electronics Quantum 2000
  - 500 μm Sample Areas
  - Maximum Depth 5.0 nm
- Qualitative - Species Present
- Quantitative - Carbon Functional Groups

ESCA

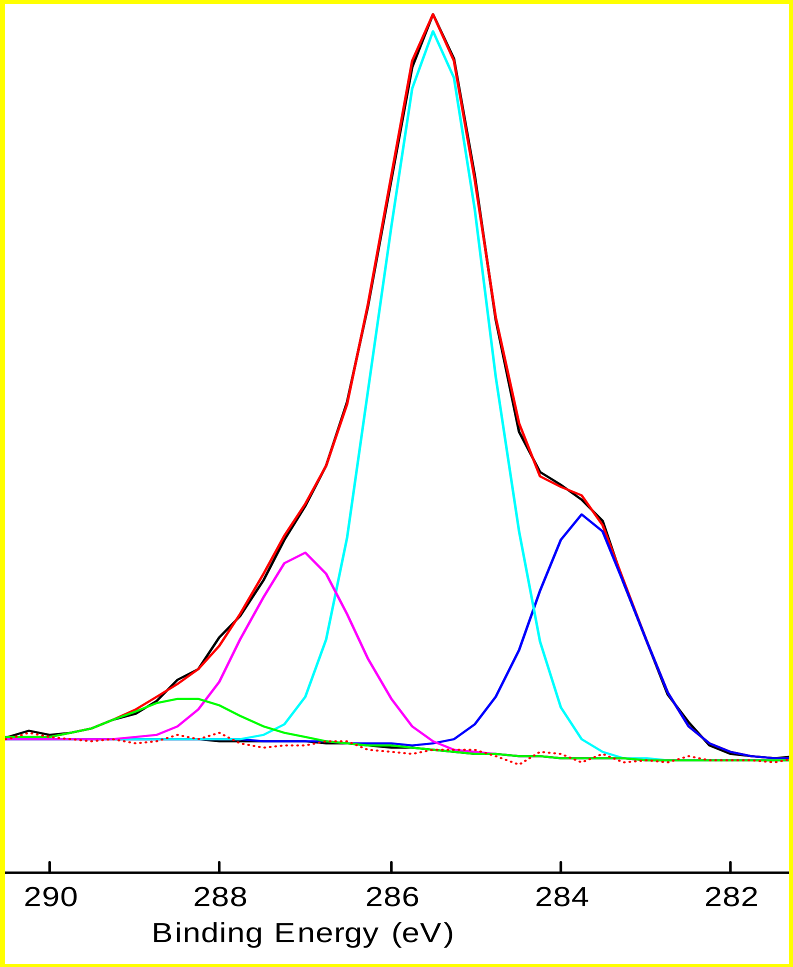




Oxidation with increased DBD treatment of BKP and TMP, only before extraction in BKP

Vander Wielen, L.C.; Ragauskas, A.J. 12th ISWPC Proceedings, Vol 1 p. 373, 2003

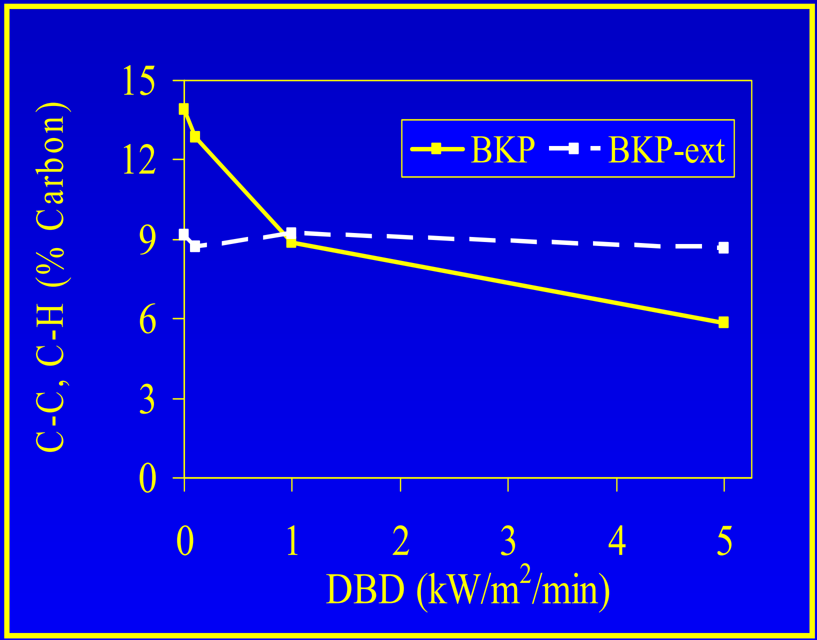
Fiber Surface Analysis - ESCA

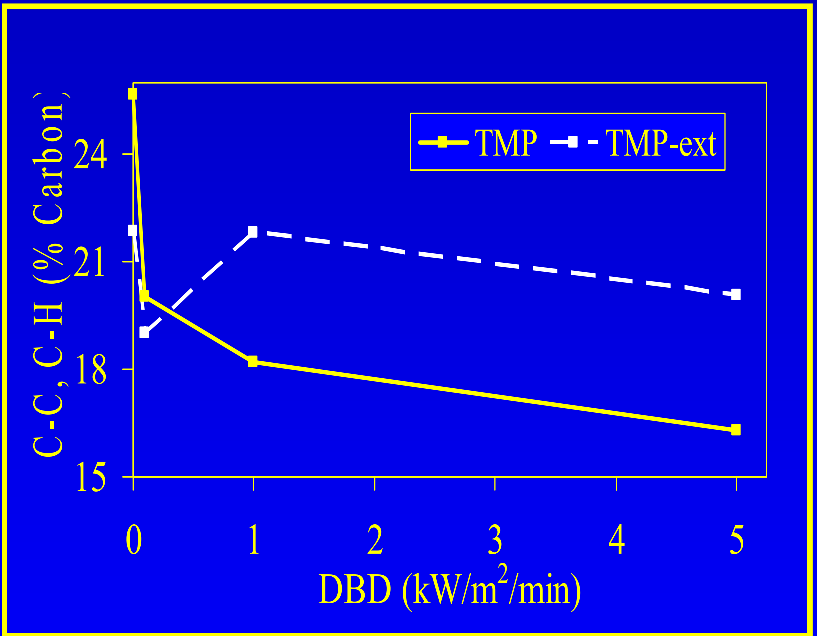


C1: C-C, C-H
C2: C-O-R
C3: O-C-O,
C=O
C4: R-O-C=O

ESCA C(1s) deconvolution peaks (Gray and Dorris, 1978)

ESCA

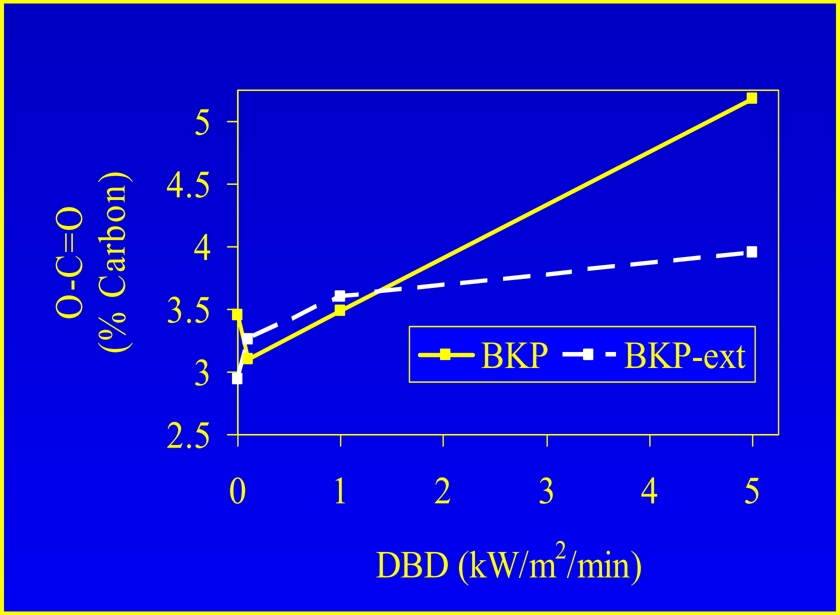


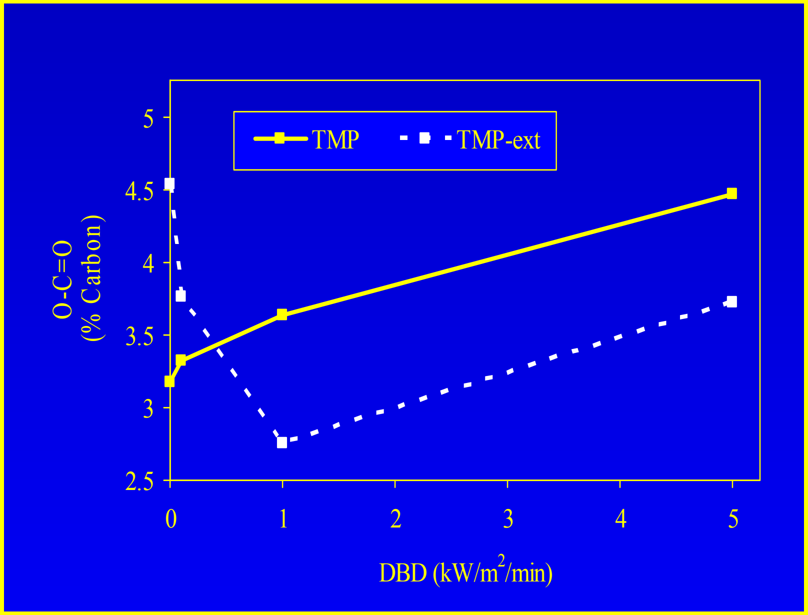


Decrease in surface extractives with increased DBD treatment of BKP and TMP.

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas. *Journal of Applied Polymer Science*, 2004.

ESCA

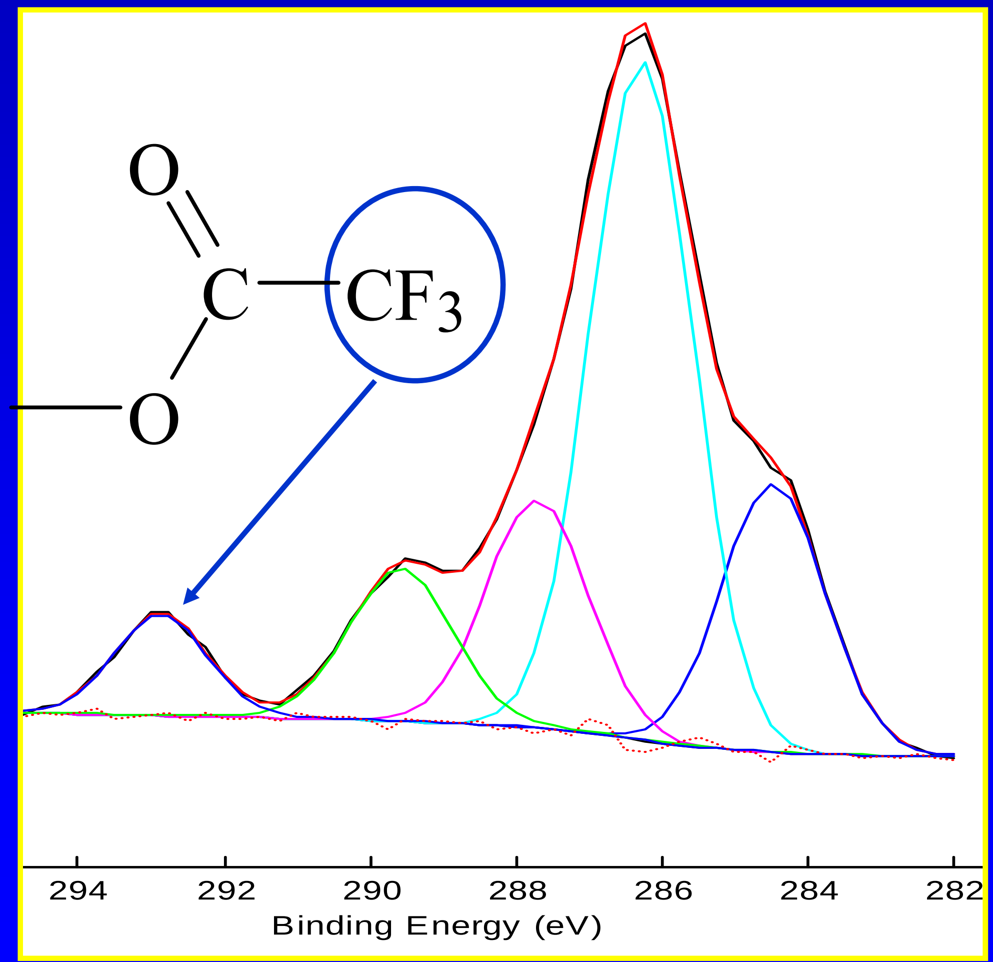




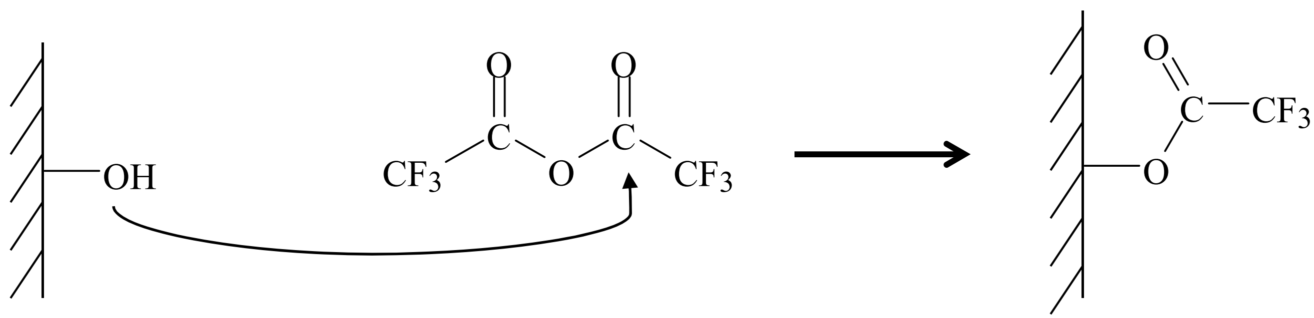
Increase on carboxylic acid or ester at increased treatment of BKP of 45-50%, 20-25% after extracted. TMP increase of 40-65%, decrease of 18% after extracted.

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas. *Journal of Applied Polymer Science*, 2004.

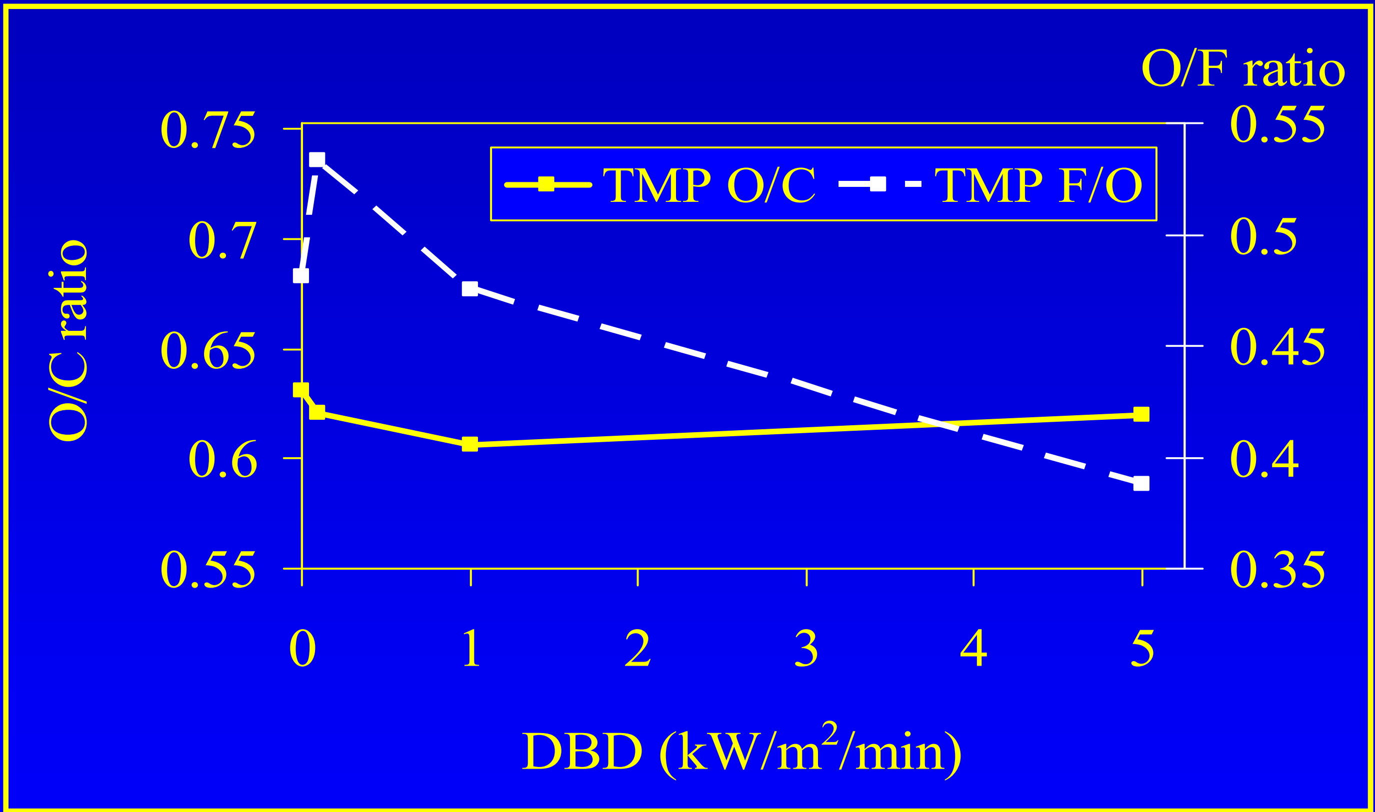
ESCA of Derivatized Fibers



Esterification with TFAA



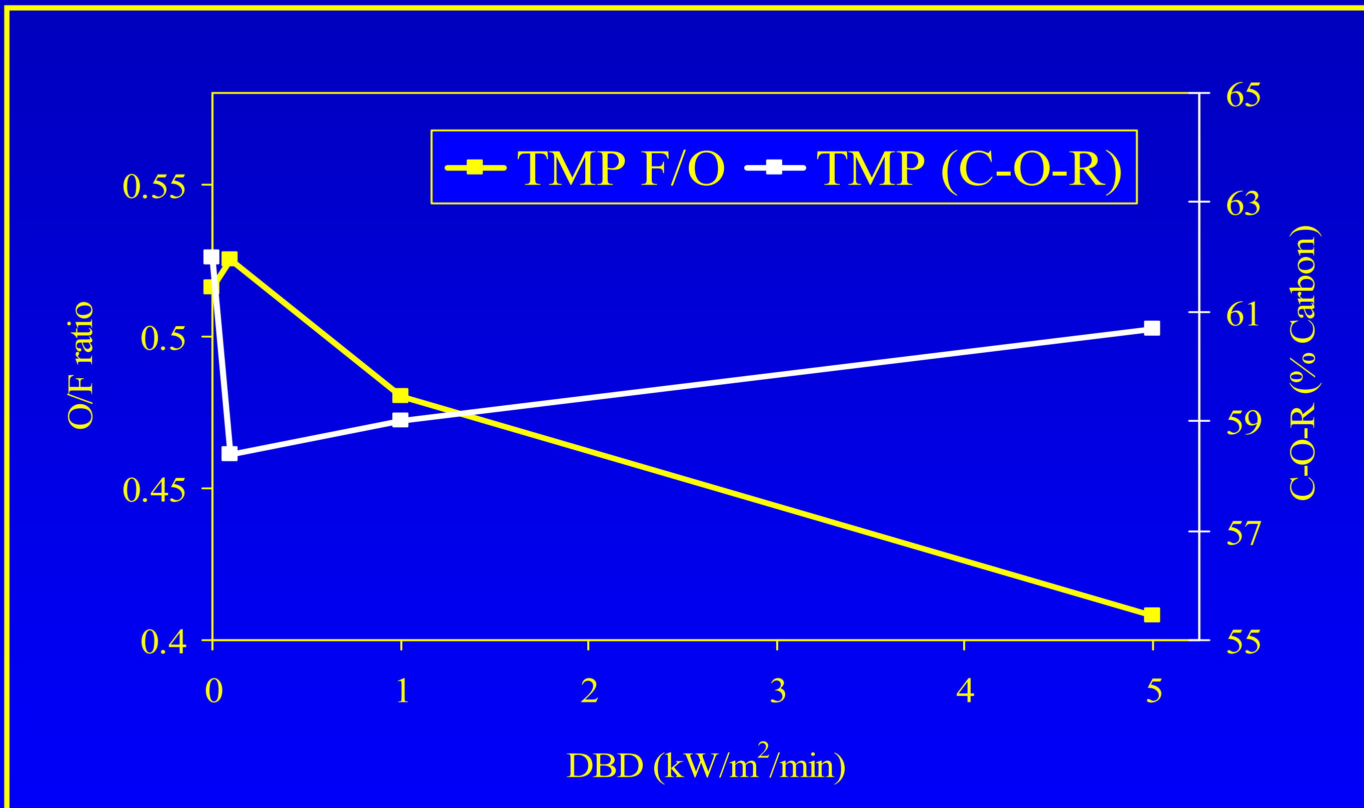
ESCA - TMP



F/O ratio of TMP increases initially, then decreases while O/C shows relatively subtle changes.

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas. Journal of Applied Polymer Science, 2004.

ESCA – Extracted TMP



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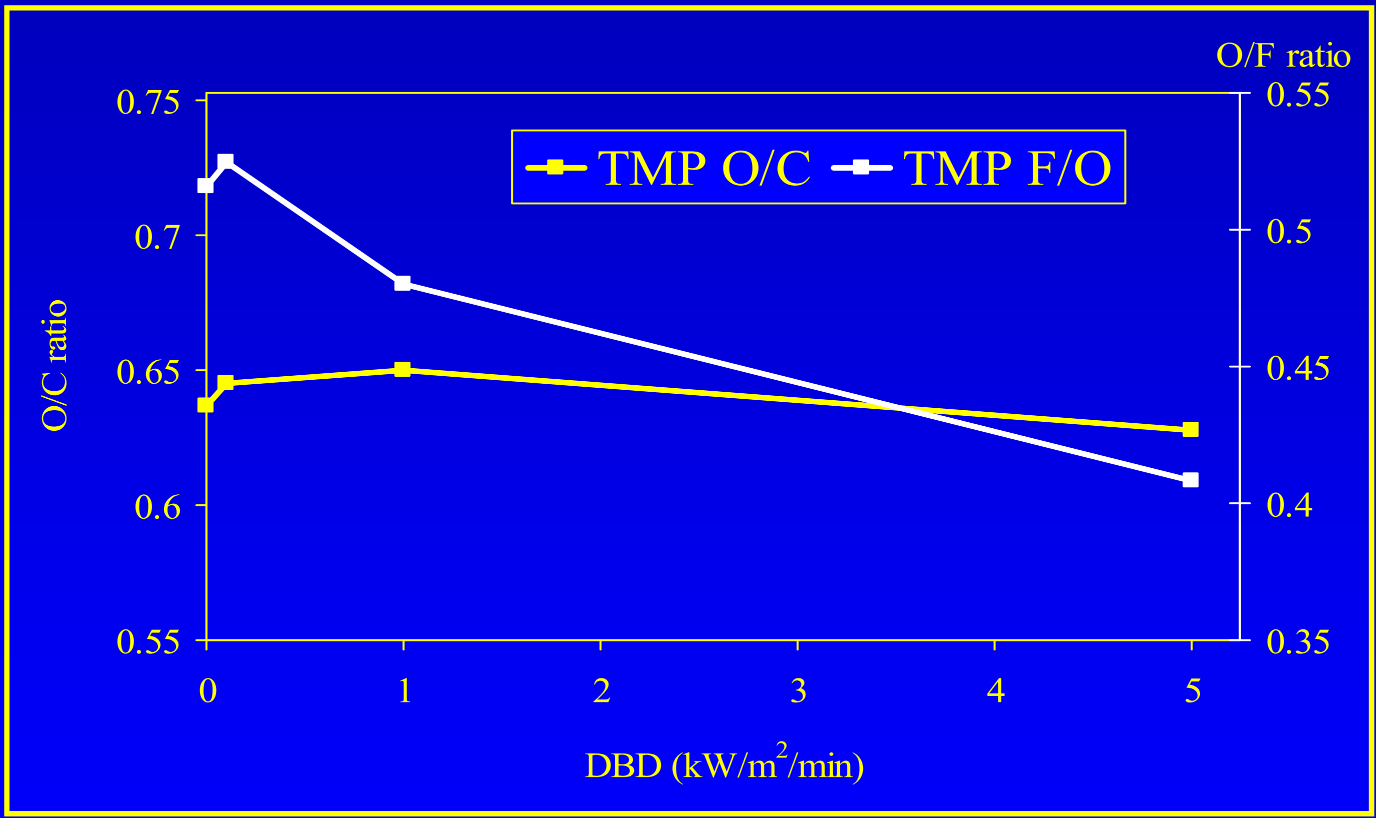
ESCA – Extracted TMP



F/O ratio of extracted TMP increases initially, then decreases while O/C shows relatively subtle changes.

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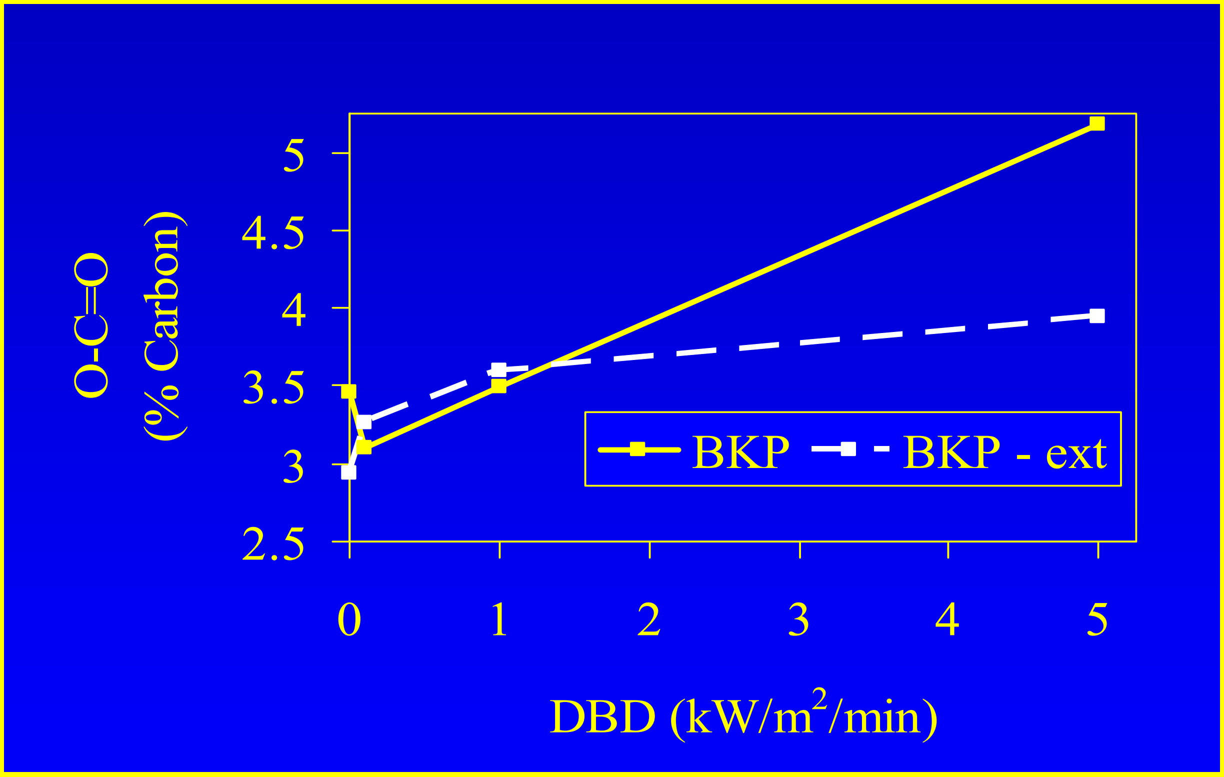
ESCA –BKP



Increase on carboxylic acid or ester at increased treatment of BKP of 45-50%, 20-25% after extracted.

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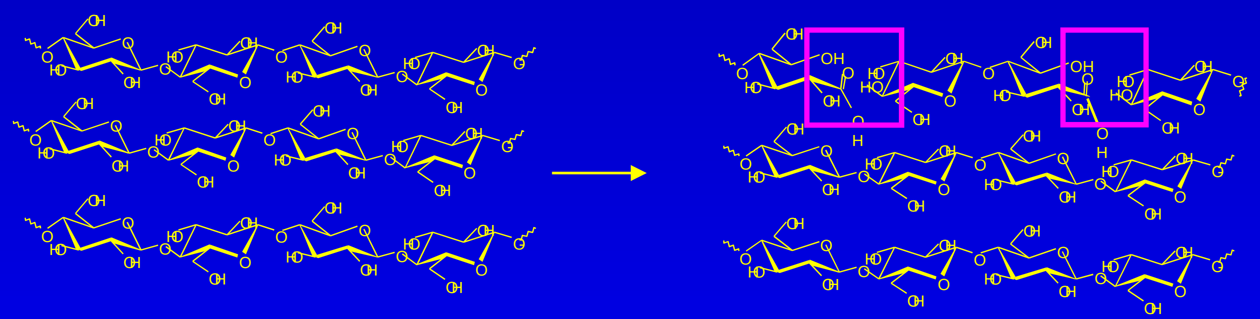
BKP Fiber Surface Chemistry - ESCA

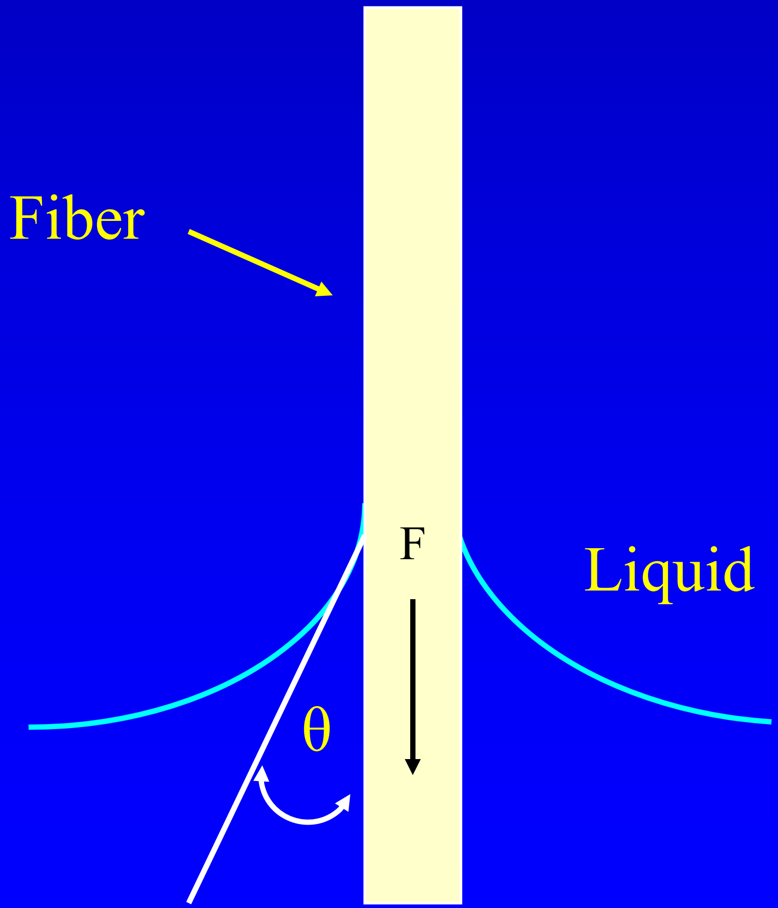


Paper

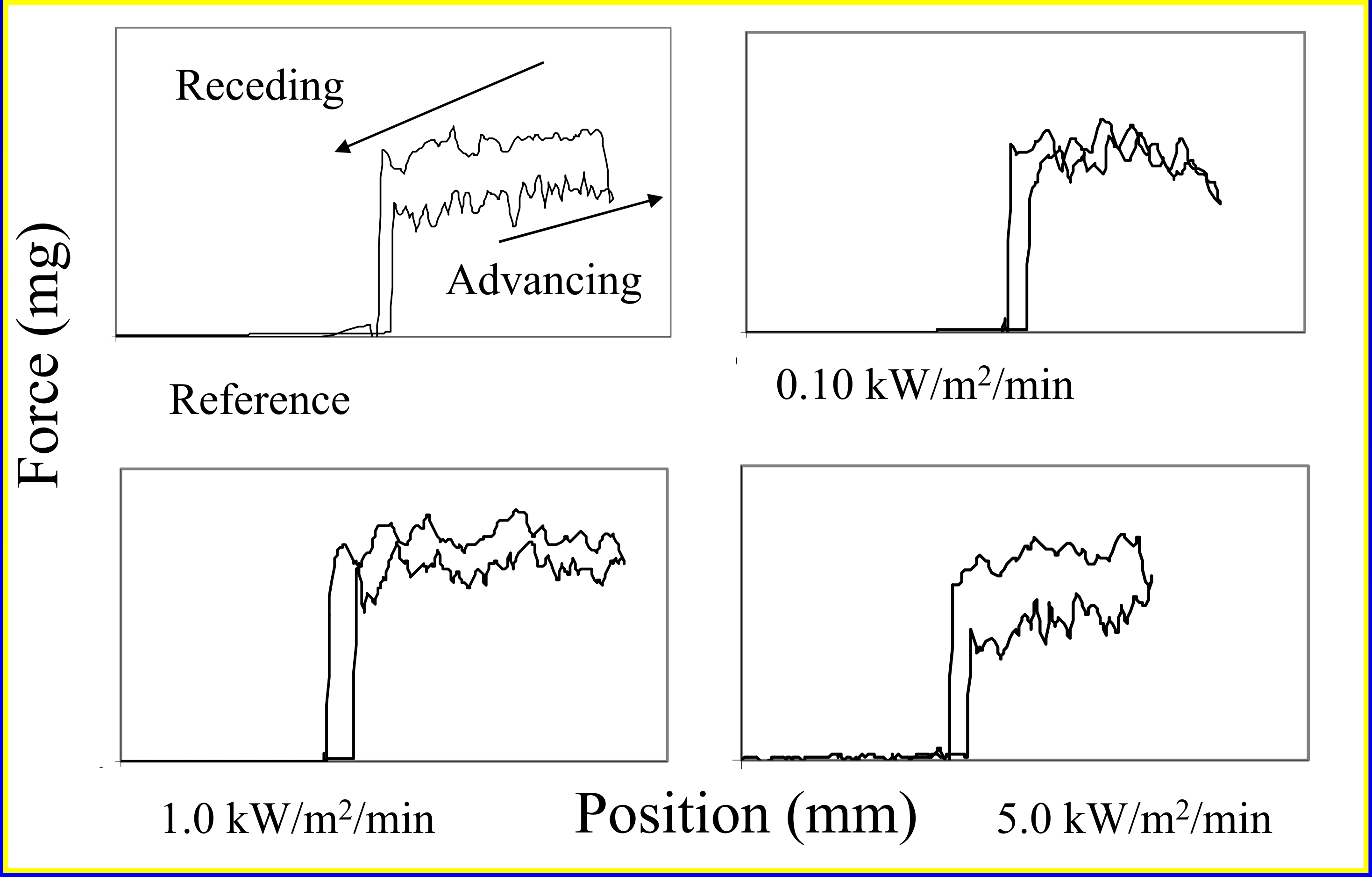
Oxidized Paper Surface

Oxidized material washes out

Wilhelmy Plate Method



Wilhelmy Plate Technique - BKP



Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas. *Journal of Applied Polymer Science*, 2004.

Wilhelmy Plate Technique – BKP

DBD Treatment ($kW/m^2/min$)	θ_a (^{o})	γ_{tot} (Jm^{-2})	γ_p (Jm^{-2})	γ_d (Jm^{-2})
0	33.6	65.1	34.5	30.6
0.1	26.1	68.4	38.1	30.3
1.0	30.4	65.3	37.7	27.6
5.0	43.2	58.3	31.1	27.1

Wettability increases at low DBD treatment, then diminishes.

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas, A.J. *Journal of Applied Polymer Science*, 2004.

Wilhelmy Plate Technique – TMP

Sample treatment ($kWm^{-2}min$)	θ_a (º)	γ_{tot} (Jm^{-2})	γ_p (Jm^{-2})	γ_d (Jm^{-2})
0	66.2	45.8	17.9	27.9
0.10	52.9	52.4	25.8	26.2
1.0	52.6	52.4	26.2	26.2
5.0	56.7	50.9	23.1	27.8

Wettability increases at low DBD treatment, then diminishes.

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas, A.J. *Journal of Applied Polymer Science*, 2004.

Objectives

- Investigate impacts on product performance
- Characterize impacts to topo-chemistry
- Explain mechanisms by which changes in physical properties occur

Wet Strength

- Wet Tensile Improvement:
  - Change in surface chemistry to prevent the interruption of bonding
  - Typical wet-strength additives:
    - Protective mechanism
      - Water affinity properties
    - Covalent bonding
      - Elastic behavior, water affinity

Espy, H. Tappi J. 1995

Wet Strength

- Wet Tensile Improvement:
  - Covalent bonding – direct evidence
    - – Ether cross-linkages in TMP
      - » ESCA - TFAA
    - – Ester cross-linkages in BKP
      - » ESCA, poly-electrolyte titration

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas. Journal of Applied Polymer Science, 2004.

Wet Strength

- Wet Tensile Improvement:
  - Indirect evidence
    - – Elastic behavior
      - » Wet-stiffening
    - – Water affinity
    - – Surface energy

Vander Wielen, L.C.; Elder, T.; Ragauskas, A.J. Cellulose, 2004.

Vander Wielen, L.C.; Östenson, M.; Gatenholm, P.; Ragauskas, A.J. Journal of Applied Polymer Science, 2004.

Conclusions: Acid Groups

- DBD increases BKP surface acids by 40-45%, net surface acids (extracted) by 20-25%
- DBD alone increases TMP surface acids by 40-65%, net decrease surface acids (extracted) of 18%
- Grafting with maleic acid increases total acids by 60%

Conclusions: Surface Chemistry

- Remove extractives
- Oxidative modification
- Surface roughens, then smoothed
- Increased, then decreased surface energy

Conclusions - Performance

- No correlation between dry tensile and increased surface acids
  - Not enough acid groups

Conclusions - Performance

- Additives did not add significant value in terms of strength properties (due to DBD treatment)
- Dramatic improvements increased in wet-tensile

Conclusions - Mechanisms

- DBD treatment results in reduced swelling, increased wet-strength and wet-stiffening due to:
  - Cross-linking of BKP via ester linkages
  - Cross-linking of TMP via ether linkages

Acknowledgments

The authors wish to acknowledge the support of the member companies of the Institute of Paper Science and Technology. Portions of this work are being used by L. Vander Wielen as partial fulfillment of the requirements for graduation from the Institute of Paper Science and Technology.