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► To cite this version:

Nathan Ferrandin-Schoffel, Charlotte Martineau-Corcós, Mohamed Haouas, Anne-Laurence Dupont, Odile Fichet. Study of the interactions and reactions in naturally aged newsprint papers strengthened with polysiloxane copolymer networks. Heritage Sciences and Technologies, Feb 2019, Paris, France. hal-02477096

HAL Id: hal-02477096

<https://hal.science/hal-02477096v1>

Submitted on 27 Nov 2020

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Study of the interactions and reactions in naturally aged newsprint papers strengthened with polysiloxane copolymer networks

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I Context

(Baty et al., 2010)

Acid hydrolysis Degradation

Cellulose + H₃O⁺ → Chain-breaking + H₃O⁺

- Natural ageing of paper in Libraries and Archives collections → lignin-rich papers: **acidity** and **brittleness**
- Need for **deacidification** & **strengthening**
- Solution: copolymerized AminoAlkylAlkoxySilanes (AAAS) (PhD C. Piovesan 2016)

II A one-pot conservation treatment

copolymerization

AP + DIA → copolymer network (copolyAAAS)



- alkoxy groups / **strengthening**
- amino groups / **deacidification** & **adsorption**

In situ copolymerization

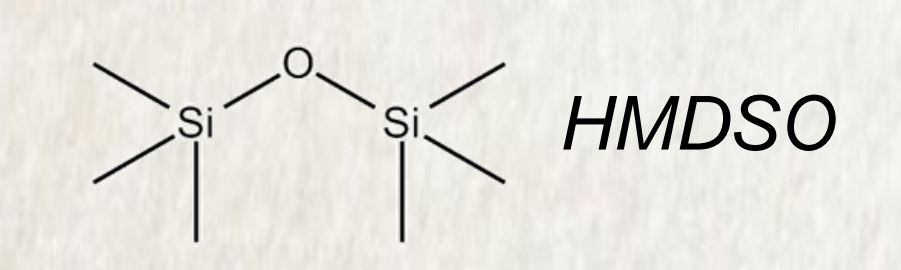
cellulose microfibrils + Water + AP + DIA → polyAP / polyDIA

Treatment

- Immersion (with solvent)
- Spray (without solvent)

 Ecospray Airbrush



 HMDSO

(Piovesan, 2014)

III Application to newsprint papers

Pulp:

- Cellulose
- Hemicelluloses
- High lignin content

Additives:

- Alum-rosin (sizing)
- Kaolin (filler)

« Journal des Fabricants de Sucre » (JFS), newsprint paper from 1922

AP/DIA Treatment (uptake UP ~7%)

Study of the mechanical properties

- Folding Endurance (FE)
- Tensile Strength

Study of the in situ polymerization

- Solid-State NMR
- FTIR (ATR mode)

IV Impact of natural ageing on a strengthened newsprint paper

Folding endurance of JFS treated AP/DIA

Untreated paper: ~94°

Paper treated AP/DIA 5/95 t0: 0° (Water is 100% absorbed!)

Paper treated AP/DIA 5/95 t0 + 3 years: ~90°

Contact angle measurements with water (10 μL)

Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) analysis of JFS treated AP/DIA 5/95 at t0

Number of double folds

Untreated AP/DIA 5/95 AP/DIA 50/50

~ -16 ppm D¹ (-SiO-Si-OH)

~ -22 ppm D² (-SiO-Si-OSi-)


Number average degree of polymerization of DIA


$\overline{DP}_n = D^2 \times \frac{2}{D^1} + 2$

$\overline{DP}_n \sim 12!$

(Souguir et al., 2012) (Pellizzi et al., 2012)

- Significant variations of mechanical properties with natural ageing
- Papers become very hydrophilic at t0 (= just after treatment), but hydrophobic character develops with time
- Low \overline{DP}_n of copolyAAAS at t0 of treatment

 **Copolymerization of AAAS : slow kinetics**

 **What are the interactions involved between AAAS and paper?**

V Interactions with paper constituents: a model study

Examples of models for lignin: vanilloids

Vanillic acid Vanillin

(+ 10 other molecular models)

(Dupont et al., 2012) (Lin & Dence, 1992)

Example of lignin in softwood pulp

AMDES (AAAS) + Vanilloid → Equimolar proportions, Room temperature

Liquid NMR (¹H, ¹³C, ²⁹Si, ¹⁵N)

FTIR (ATR mode)

a) **Example of vanillin:**

(aromatic)

imine

~ -13.5 ppm D¹ (-SiO-Si-OEt)

~ -19.5 ppm Cyclic tetramer

~ -22 ppm D² (-SiO-Si-OSi-)

(Bennevault-Celton et al., 2012)

Formation of a Schiff base

Covalent bond between AMDES & vanillin

b) **Example of vanillic acid:**

Vanillic acid

Vanillic acid + AMDES

Formation of an ammonium salt

Ionic bond between AMDES & vanillic acid

Acknowledgements

We thank the **Foundation for Cultural Heritage Sciences** for N. Ferrandin-Schoffel's doctoral grant (Co-Sil-Bib project).

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VI Conclusion

- Identification of several types of interactions between AMDES and molecular lignin models: possible extrapolation of reaction mechanisms between AAAS and newsprint papers constituents?
- Estimation of the \overline{DP}_n of copolyAAAS in situ in paper: evidence of slow polymerization kinetics

More papers tested (solid state NMR) and current research on catalysts