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

N. Ferrandin-Schoffel^{1,3}, C. Martineau-Corcoss², M. Haouas², A.-L. Dupont¹, O. Fichet³

¹Centre de Recherche sur la Conservation des Collections (CRC, CNRS USR 3224), Muséum National d'Histoire Naturelle, 36 rue Geoffroy St Hilaire 75005 Paris, France

²Institut Lavoisier de Versailles (ILV, UMR 8180), Université de Versailles Saint-Quentin, 45 avenue des Etats-Unis, 78035 Versailles, France

³Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI, EA 2528), Institut des Matériaux, Université de Cergy-Pontoise, 5 mail Gay-Lussac, Neuville sur Oise 95031 Cergy-Pontoise cedex, France

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 + H₂O → copolymer network (copolyAAAS)

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



III Application to newsprint papers

In situ copolymerization

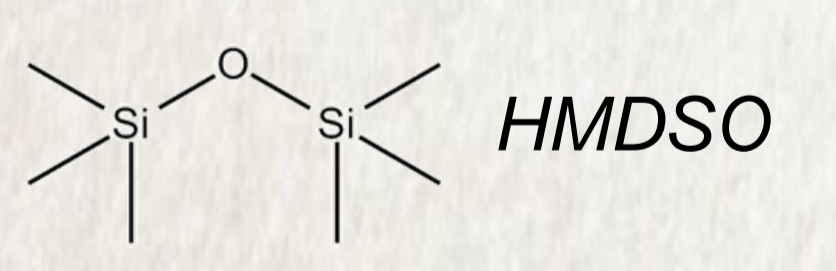
cellulose microfibrils + Water + AP + DIA → polyAP / polyDIA

Treatment

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

1. Immersion (with solvent) 2. Spray (without solvent)



(Piovesan, 2014)

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)

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Contact : nathan.ferrandin-schoffel@mnhn.fr
Phone : +33 1 40 79 53 06

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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: **Water is 100% absorbed!** (0°)

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

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)

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

Liquid NMR (¹H, ¹³C, ²⁹Si, ¹⁵N) **FTIR (ATR mode)**

a) **Example of vanillin:**

- ~ -13.5 ppm D¹ (-SiO-Si-OEt) (aromatic)
- ~ -19.5 ppm Cyclic tetramer
- ~ -22 ppm D² (-SiO-Si-OSi-)

- Formation of a **Schiff base**
- Covalent bond between AMDES & vanillin

b) **Example of vanillic acid:**

- Formation of an **ammonium salt**
- Ionic bond between AMDES & vanillic acid

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