

CELLULOSE MODIFICATION BY CROSSLINKING
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New crosslinked siloxane-cellulose polyester materials were synthesized by direct solution polycondensation, at room temperature, starting from cellulose acetate and two siloxane diacids. Dicyclohexylcarbodiimide (DCC) was used as activator and 4-(N,N-dimethylamino)pyridinium-p-toluenesulfonate (DPTS) as catalyst. IR spectroscopy was used for the characterization of polyesters. The obtained compounds were insoluble in common organic solvents, due to crosslinking. The morphology of the obtained materials was observed by SEM, while surface composition was determined by EDX analysis. The water vapor sorption-desorption behavior of the crosslinked materials was studied by dynamic vapor sorption (DVS) analysis, and the results were compared with those of the starting cellulose acetate.

Keywords: cellulose acetate, siloxane, crosslinking, polycondensation

INTRODUCTION

Cellulose-based materials are widely used in everyday life. However, water and humid environments cause problems for these materials, such as loss of dimensional stability, poor wet stiffness, and tendency to creep under load. It is therefore important to find alternatives for crosslinking cellulose.

Chemical crosslinking leads to the improvement of the wet state properties of cellulose materials,¹ because the covalent bridges between cellulose chains limit the swelling of cellulose and thus protect the hydrogen bonds against the disrupting action of the water molecules.² Classic cellulose crosslinking systems, such as compounds using N-methylol chemistry, release formaldehyde, known as a human carcinogen.¹ Siloxanes are used on a large scale in many different fields – coatings,³⁻⁵ biomaterials and materials for medical applications,⁶⁻⁸ cosmetics, sensors and optical materials,^{9,10} etc. This class of chemicals is water-repellent, with good resistance in wet environments, besides, siloxane polymers are not toxic for humans.

The presence of siloxane chains could determine changes in the properties of cellulose materials, such as an improvement of the thermal-oxidative stability, increased flexibility, antifouling, resistance to UV radiations, etc.¹¹⁻¹⁴

The present study investigates new cellulose-based materials containing siloxane either in the side chain or as siloxane-cellulose backbones. Crosslinking of cellulose acetate with a substitution degree of 1.2 with siloxanes containing Si-H groups was already reported.^{15,16} In the presence of a Pt-based catalyst, dehydrocoupling reactions occurred between the residual C-OH groups and Si-H, forming Si-O-C bridges between cellulose and siloxane derivatives. As known, such bonds are susceptible to hydrolysis, limiting the field of applications of these networks. Based on our previous results on the modification of surface properties of crosslinked cellulose containing short siloxane segments, the surface properties of the new compounds have been investigated by SEM-EDX and dynamic

water vapour sorption. The obtained results confirmed that short siloxane moieties, such as disiloxane, may induce rather important modifications in surface composition and, hence, in surface properties. This represents an interesting method in applications concerning modification of surface properties and improvement of the wet-state mechanical properties of cellulose and of cellulose-based materials.

The paper reports the synthesis of siloxane-crosslinked cellulose polyesters by direct polycondensation in solution, at room temperature, using dicyclohexylcarbodiimide (DCC) as an activating agent, and 4-(N,N-dimethylamino)pyridinium - p -toluenesulfonate (DPTS) as catalyst. Siloxane diacids with various chain lengths were used as reaction partners for cellulose acetate, and the influence of siloxane segment length on the final properties of the polymers was investigated.

EXPERIMENTAL

Materials

Cellulose acetate, $C_6H_{8.8}O_{3.8}(OCOCH_3)_{1.2}$, CA, supplied by Fluka, had the following characteristics: DS = 1.2; $d_4^{20} = 0.996$; purity > 99%.

Acetone (Chimopar-Romania) and N,N-dimethylformamide (DMF) (Fluka) purity > 99.9% – were used after drying by standard methods.

1,3-bis(cyanopropyl)tetramethyldisiloxane, dicyclohexylcarbodiimide (DCC), 4-(N,N-dimethylamino)pyridine (DMAP) and p-toluenesulfonic acid (PTS) were high-purity commercial products, used as received.

1,3-bis(carboxypropyl)tetramethyldisiloxane, S1, was prepared from 1,3-bis(cyanopropyl)tetramethyldisiloxane by hydrolysis.¹⁷ α,ω -bis(carboxypropyl) oligosiloxane, S2, was obtained from S1, by equilibration with octamethylcyclotetrasiloxane, in a heterogeneous medium, according to the procedure described in a previous paper.¹⁸ Polydispersity of the obtained oligomer was of about 1.4 and molecular weight was of 737, as determined by ¹H-NMR.

4-(N,N-dimethylamino)pyridinium-p-toluenesulfonate catalyst, DPTS, m.p. = 176 °C, was synthesized according to a known method.¹⁹

Equipments

Fourier transform infrared spectra (FT-IR) were obtained on a Bruker Vertex 70 FT-IR analyzer. Analyses were performed in the 400-4000 cm^{-1} range, at room temperature, with 2 cm^{-1} resolution and accumulation of 32 scans.

Measurements for dynamic vapour sorption and sorption hysteresis were performed with an

IGAsorp Dynamic Vapour Sorption apparatus with the following characteristics: minimum gas pressure of 2 bar; resolution of 0.1 μg for 100 mg and sample containers made out of stainless steel micron-sized mesh. Before sorption measurements, the samples were dried at 25 °C in a dry nitrogen flow (250 mL/min) until the weight of the sample was in equilibrium at a relative humidity (RH) less than 1%.

Electron microscopy investigations were performed on a Quanta 200 type Scanning Electron Microscope (SEM) operating at 510 kV with backscattered electrons in low vacuum mode, equipped with an Energy Dispersive X-Ray system (EDX) for qualitative and quantitative analysis and elemental mapping, which allowed determination of surface composition.

The silicon content was determined according to a known procedure,²⁰ i.e. disintegration with sulfuric acid and calcination at 900 °C up to constant weight.

Procedure

Cellulose-disiloxane polyester

Cellulose acetate (0.5 g, 2.4 mmol anhydroglucose units) and 1,3-bis(carboxypropyl)tetramethyldisiloxane (0.3 g, 1.2 mmol) were dissolved in 10 mL dry DMF, in a reaction vessel. DCC (0.25 g, 1.2 mmol) and DPTS (0.03 g, 0.1 mmol) were then added. The mixture was stirred at room temperature for 12 h, a solid white gel, insoluble in usual solvents, being formed. After filtration, the crude product was washed with distilled water, dried and then washed with dry acetone. The washing procedure was repeated for eliminating the traces of urea from the crosslinked product (P1).

Cellulose-oligosiloxane polyester

Cellulose acetate (0.5 g, 2.4 mmol anhydroglucose units) and α,ω -bis(carboxypropyl)oligosiloxane (0.18 g, 0.6 mmol) were dissolved in 10 mL dry DMF, in a reaction vessel. DCC (0.25 g, 1.2 mmol) and DPTS (0.03 g, 0.1 mmol) were added. A lower ratio of siloxane/cellulose acetate was used in the reaction, no crosslinking of all available cellulose OH groups being necessary. The mixture was stirred at room temperature for 48 h. After this interval, the product, still in solution, was poured in a Petri dish to form a film, after slow evaporation of the solvent. The crude product was washed with distilled water and dried, then washed with dry acetone and dried again. The washing procedure was repeated to eliminate all urea traces from the product (P2).

Test reaction

Cellulose acetate (0.5 g, 2.4 mmol anhydroglucose units) was dissolved in 10 mL dry DMF, then DCC (0.25 g, 1.2 mmol) and DPTS (0.03 g, 0.1 mmol) were added. The

mixture was stirred at room temperature for 48 h, then poured in a Petri dish. The crude product was washed with distilled water, dried and washed with dry acetone, then dried again, to eliminate any urea traces.

RESULTS AND DISCUSSION

One polyester with 1,3-bis(carboxypropyl)tetramethyldisiloxane (P1) and one with an α, ω -bis(carboxypropyl)oligosiloxane (P2) were synthesized, according to Figure 1.

Synthesis of cellulose-based polyesters containing siloxane sequences has been achieved by direct polycondensation reactions in solution. The activating system for this reaction is based on DCC as activating agent and DPTS as catalyst. This procedure has significant advantages: mild reaction conditions (ambient temperature) and neutral reaction environment. The avoidance of acid chlorides and high temperatures, which affect the stability of certain siloxane compounds, recommends it for large-scale synthesis. Previous papers reported the use of the same method for the synthesis of siloxane-organic polyesters with azomethine groups and of azobenzene-containing siloxane polyesters.^{21,22}

To check the possible changes occurring in the cellulose structure, CA was treated in a test reaction as in polycondensation reactions, yet without adding carboxy-siloxane compounds. The IR spectra of the starting CA and CA after treatment with DCC and DPTS showed no significant differences; the ester carbonyl band had the same position, (*i.e.* 1757 cm^{-1}) and intensity.

The final products were characterized by FT-IR spectroscopy. Besides the bands characteristic of the starting CA (3484 cm^{-1} – νOH , 1754 cm^{-1} – $\nu\text{C=O}$ ester, 1240 cm^{-1} – $\nu\text{C-O}$ carboxylate, 1050 cm^{-1} – νCOC),²³ the presence of siloxane characteristic bands may be observed in the reaction products, at 800 cm^{-1} (CH_3 rocking and Si-CH stretching in SiCH_3), 1030-1090 (Si-O-Si), 1260 (sym. CH_3 in Si-CH_3),²⁴ although partial overlapping occurs in the two last cases (Fig. 2a). The most important evidence for the formation of new products is the presence of the SiCH_3 absorption band at 800 cm^{-1} , together with the disappearance of the carboxylic acid band recorded in the starting disiloxanes at 1714 cm^{-1} (Fig. 2b). The OH band in CA at 3484 cm^{-1} seriously diminished the reaction products, confirming

the participation of these groups at the polycondensation reaction.

The crosslinked cellulose-siloxane polyesters are not soluble in organic solvents, from chloroform to DMF, being also insoluble in solvents specific to cellulose, like DMSO-TBAF (dimethylsulfoxide-tetra-n-butylammonium fluoride).

The morphology of the obtained crosslinked cellulose materials was observed by SEM, in comparison with the starting CA (film obtained from DMF). Representative images describing the new materials are shown in Figure 3. The new materials, showing a typical aspect, with pores and fibrillar structures, clearly differ from the cellulose acetate treated under the same conditions.

The surface properties of this type of polyesters are interesting for coatings and gel-based materials. Polysiloxanes impart hydrophobicity or water repellency. These properties have been emphasized in block copolymers and blends, and it is interesting to study the effect of siloxane units on the surface properties of cellulose.

Surface composition of the crosslinked cellulose materials has been determined by EDX, within SEM analysis. For each sample O, C and Si were detected. The results of the quantitative surface analysis are listed in Table 1, for both weight (wt%) and atomic (At%) ratios. The Si content was also determined by calcinations, the results obtained being 2.2% for P1 and 5.7% for P2, respectively. These values are very close to those obtained for the surface (taking into account that H is not detected in EDX).

Based on Si% in bulk, as obtained by the calcination method, the crosslinking degree was estimated as follows:

$$N = 0.5 \cdot \frac{\left[\frac{28 \cdot n \cdot 100}{\text{Si}\%} - \text{MS} \right]}{212}$$

where: N – number of cellulose anhydroglucose acetate units between crosslinkings;

n – number of Si atoms in the crosslinker;

MS – molecular weight of the crosslinker.

The number of cellulose anhydroglucose units between crosslinks obtained on the basis of such reasoning, was 5.5 for P1 and 7.7 for P2, respectively.

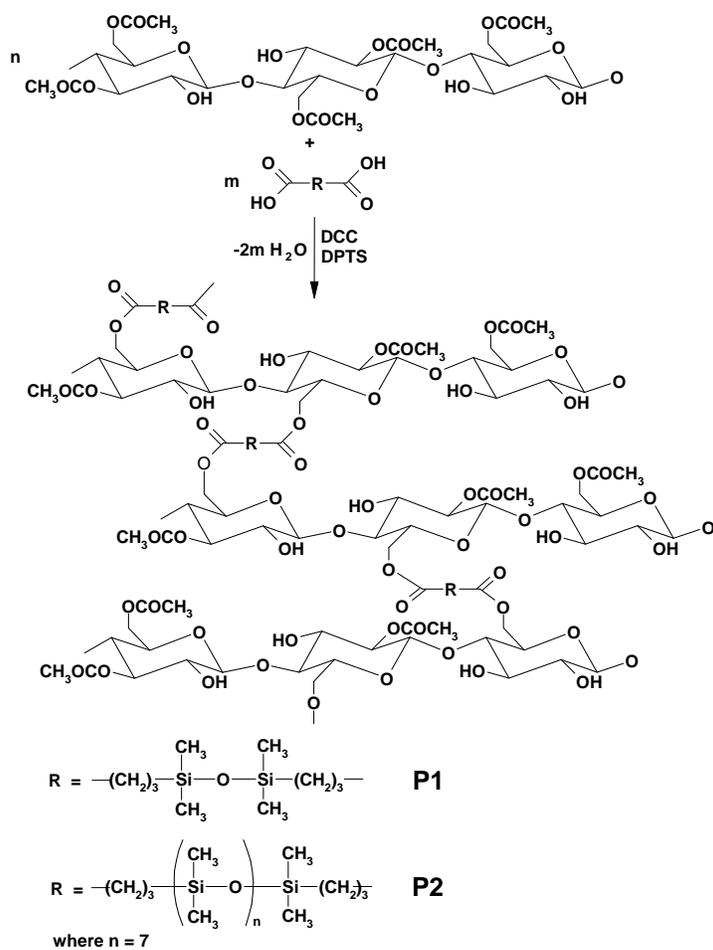


Figure 1: Reaction path for polyesters

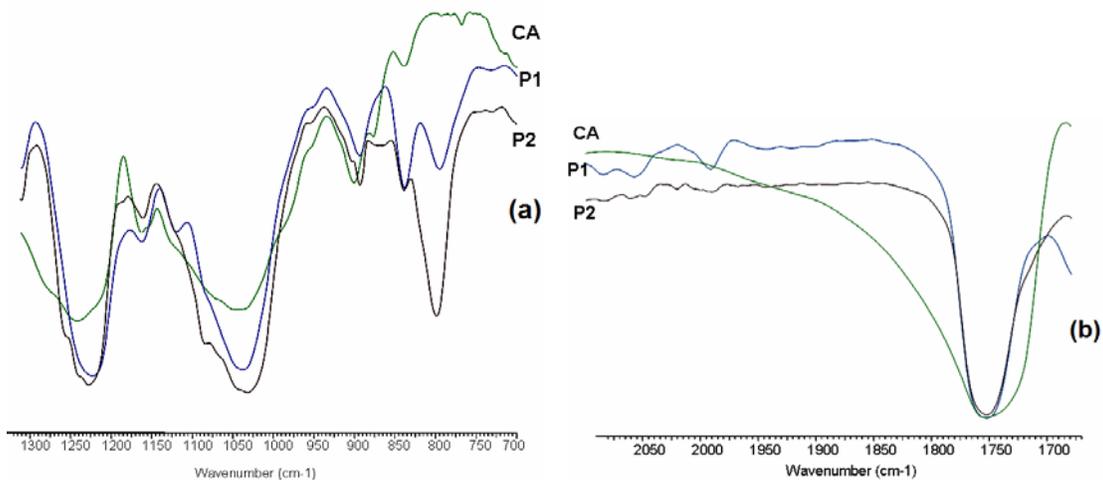


Figure 2: IR spectra of starting CA and resulting crosslinked materials, (a) showing presence of siloxane bands in the 700-1300 cm⁻¹ region; (b) carbonyl region, showing presence of ester groups and absence of carboxyl bonds

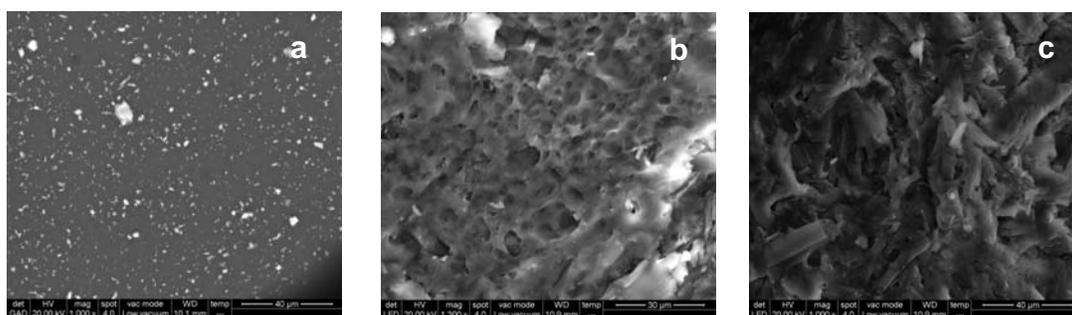


Figure 3: SEM images of CA film (a) and crosslinked materials with disiloxane (b) and oligosiloxane (c)

Table 1
Surface composition from EDX measurements

Sample	C		O		Si	
	wt%	At%	wt%	At%	wt%	At%
P1	70.13	76.32	27.8	22.71	2.07	0.96
P2	67.79	75.22	26.49	22.06	5.72	2.71

Figure 4 shows water sorption at 25 °C, expressed as the total water uptake per sample mass, as a function of environmental relative humidity (sorption isotherms) for the obtained materials, compared to CA. The shape of water vapor sorption isotherms and the amount of sorbed water are determined by the characteristics of the sample. Physically bound water can be adsorbed to the surface or in the structure of the material or could be capillary condensed in pores. The water sorption capacity of CA (cellulose acetate) has the highest value (12.4%), which can be explained by the presence of the hydroxyl residual groups in cellulose acetate, which determines a slightly hydrophilic character. The siloxane-modified materials

gave values around 6%, very close to each other, showing that the presence of a disiloxane unit could have the same effect as a longer siloxane. This is an expected result since, in this case, crosslinking means, on the one hand, decrease of the OH groups number and, on the other, introduction of a hydrophobic material in the cellulose structure. The shapes of the moisture sorption isotherms are similar to those characteristic of mesoporous materials²⁵ (type IV – with low sorption at low humidities, moderate sorption at average humidities and rapidly increasing water sorption at high humidities). The rate of desorption was slower than that of sorption, forming a small hysteresis loop.

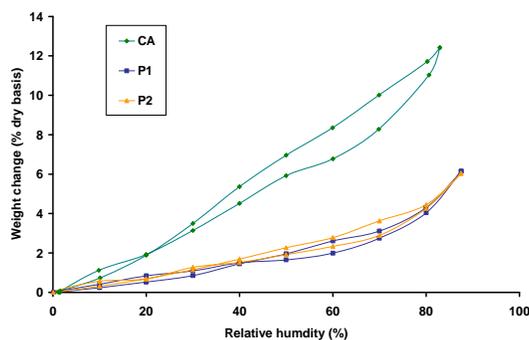


Figure 4: Rapid water vapor sorption isotherms

CONCLUSIONS

New crosslinked siloxane-cellulose polyesters were obtained by crosslinking cellulose acetate with siloxane diacids of different molecular weights, in solution, by

direct polycondensation reactions, at room temperature.

Surface composition, as determined by EDX, showed practically the same Si content as in the bulk; based on these values, a number of 5.5 and 7.7 units of cellulose

acetate between the crosslinking nodes was estimated. The water sorption properties were significantly influenced by the presence of siloxane moieties. A lower water sorption capacity was found for siloxane-containing polyesters, compared to the cellulose model polymer, due to the presence of both crosslinking and siloxane.

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REFERENCES

- ¹ J. P. Hauser, C. B. Smith and M. M. Hashem, *AUTEX Research J.*, **4**, 95 (2004).
- ² D. F. Caulfield, *Tappi J.*, **77**, 205 (1994).
- ³ B. Twomey, D. Dowling, G. Byrne, L. O'Neill and L.-A. O'Hare, *Plasma Process Polym.*, **4**, S450 (2007).
- ⁴ N. B. Madsen, PhD Dissertation, Roskilde, Denmark, 1999, p. 3.
- ⁵ M. Bengtsson, N. M. Stark and K. Oksman, *Polym. Composites*, **27**, 184 (2006).
- ⁶ L. Ren, K. Tsuru, S. Hayakawa and A. Osaka, *Biomaterials*, **23**, 4765 (2002).
- ⁷ L. Liu and H. Sheardown, *Biomaterials*, **26**, 233 (2005).
- ⁸ M. Cazacu, C. Racles, A. Vlad, M. Antohe and N. Forna, *J. Compos. Mater.*, **43**, 2045 (2009).
- ⁹ S. G. Ignatov, J. A. Ferguson and D. R. Walt, *Biosens. Bioelectron.*, **16**, 109 (2001).
- ¹⁰ C. E. Brunchi, A. Filimon, M. Cazacu and S. Ioan, *High Perform. Polym.*, **21**, 31 (2009).
- ¹¹ O. Fichet, F. Vidal, J. Laskar and D. Teyssié, *Polymer*, **46**, 37 (2005).
- ¹² O. Fichet, F. Vidal, J. Laskar and D. Teyssié, *Polymer*, **47**, 3747 (2006).
- ¹³ E. Ferjani, M. Mejdoub, M. S. Roudesli, M. M. Chehimi, D. Picard and M. Delamar, *J. Membrane Sci.*, **165**, 125 (2000).
- ¹⁴ C. Racles and T. Hamaide, *Macromol. Chem. Phys.*, **206**, 1757 (2005).
- ¹⁵ G. Stiubianu, M. Cazacu, A. Nicolescu, V. Hamciuc and S. Vlad, *J. Polym. Res.*, **17**, 837 (2009).
- ¹⁶ G. Stiubianu, C. Racles, M. Cazacu and B. C. Simionescu, *J. Mater. Sci.*, **45**, 4141 (2010).
- ¹⁷ J. E. Mulvaney and C. S. Marvel, *J. Polym. Sci.*, **50**, 541 (1961).
- ¹⁸ M. Cazacu, M. Marcu, A. Vlad, D. Caraiman, C. Racles, *Eur. Polym. J.*, **35**, 1629 (1999).
- ¹⁹ J. S. Moore and S. I. Stupp, *Macromolecules*, **23**, 65 (1990).
- ²⁰ M. D. Gaul and N. C. Angelotti, in "The Analytical Chemistry of Silicones", edited by Smith A. Lee, John Wiley and Sons, New York, 1991, p. 181.
- ²¹ C. Racles, V. Cozan, M. Cazacu, E. Foldes and I. Sajo, *High Perform. Polym.*, **14**, 397 (2002).
- ²² C. Racles, D. Filip, M. Cazacu, V. Cozan, A. Tóth and G. Ioanid, *Macromol. Chem. Phys.*, **207**, 1599 (2006).
- ²³ L. M. Ilharco and R. Brito de Barros, *Langmuir*, **16**, 9331 (2000).
- ²⁴ Kirill Efimenko, William E. Wallace and Jan Genzer, *J. Colloid Interf. Sci.*, **254**, 306 (2002).
- ²⁵ Eng-Poh Ng and S. Mintova, *Micropor. Mesopor. Mat.*, **114**, 1 (2008).