

# Investigation of the hydrolysis of (3-triethoxysilylpropyl)succinic acid anhydride by means of FT-IR

Christian Schramm · Beate Rinderer

Received: 13 February 2008 / Accepted: 21 March 2008 / Published online: 10 April 2008  
© Springer Science+Business Media, LLC 2008

**Abstract** The kinetic data (rate constant, Arrhenius activation energy, frequency factor) of the hydrolysis reaction of the anhydride moiety of (3-triethoxysilylpropyl)succinic acid anhydride (TESP-SA) were investigated by means of FT-IR monitoring the decrease of the carbonyl stretching band at  $1778\text{ cm}^{-1}$ . The reaction had been conducted in an excess of water under acidic conditions (pseudo-first order reaction). In addition, the application of TESP-SA to cotton fabrics in conjunction with sodium hypophosphite as curing catalyst at elevated temperature ( $180\text{ °C}$ , 90 s) was tested. The dry crease recovery angle proved that no crosslinking reaction of the cellulose chains could be observed.

## Introduction

The sol–gel process is an excellent technique to fabricate materials with novel properties. During the sol-gel process nanometer-sized particles are produced by hydrolysis of metal or semimetal alkoxides. Subsequently these nanoparticles react with one another thus forming a gel consisting of a three-dimensional network that is filled with a liquid. The latter is removed by a drying process. In the sol–gel chemistry metal alkoxides are normally used as precursors. These metal organic compounds have an organic ligand attached to a metal via a metal–oxygen–

carbon linkage. Among these precursors the silicon alkoxides are those of highest interest. The alkoxy group of the silicon alkoxide hydrolyzes to particles containing Si–OH groups which condensate to siloxanes [1–3]. The substitution of one alkoxy group by an organic functionality results in the formation of an organotrialkoxy silane. The organic group can consist of various units such as amino, epoxy, glycidoxy, isocyanato, anhydride, mercapto, or vinyl group [4–6]. The metal-oxo-clusters thus obtained can be applied in various areas [7–11].

The objective of the present work was to investigate the hydrolysis reaction of (3-triethoxysilylpropyl)succinic acid anhydride (TESP-SA) in the presence of an excess of water by means of FT-IR (Fig. 1), since the conversion of the anhydride functionality into the corresponding carboxylic groups is of high interest. The decrease of the vibration band of the anhydride component can easily be monitored. Furthermore we also investigated the reaction of a hydrolyzed TESP-SA solution with a cellulosic material in combination with the phosphorus-containing catalyst sodium hypophosphite monohydrate at elevated temperatures, since polyfunctional carboxylic acids are capable of reacting with cellulosic material by means of a proper catalyst such as phosphorus-containing salts [12–14].

## Experimental

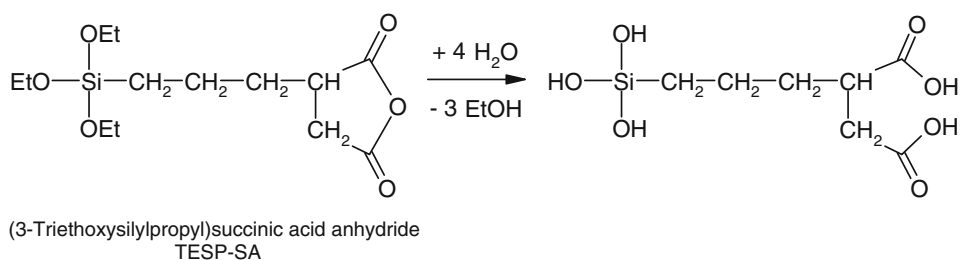
### Apparatus

FT-IR measurements were conducted with a Bruker Vector 22 equipped with a LADTGS detector. OPUS NT version 3 was used for data acquisition and data evaluation. The ATR measurements of the hydrolysis solutions were measured using a Miracle Single Reflection Horizontal

C. Schramm (✉) · B. Rinderer  
Research Institute of Textile Chemistry and Textile Physics,  
University of Innsbruck, Höchsterstrasse 73, 6850 Dornbirn,  
Austria  
e-mail: christian.schramm@uibk.ac.at

B. Rinderer  
e-mail: beate.rinderer@uibk.ac.at

**Fig. 1** Hydrolysis reaction of TESP-SA



ATR (PIKE Technologies) applying a trough insert for investigating liquid samples. A diamond crystal was used throughout the study. Usually 20 scans were recorded.

#### Reagents

(3-Triethoxysilylpropyl)succinic acid anhydride was granted by Wacker-Chemie GmbH, Burghausen, Germany. Sodium hypophosphite monohydrate,  $\text{NaH}_2\text{PO}_2 \times \text{H}_2\text{O}$  puriss (SHP), was supplied by Merck, Darmstadt, Germany.

#### Hydrolysis of TESP-SA

Ten mL TESP-SA was placed in a three-necked round bottom flask and dissolved in 10 mL absolute ethanol. The mixture was allowed to warm up to the corresponding reaction temperature. Subsequently, water was added to the reaction mixture and after 3 min a small amount of the solution was removed and placed on the liquid device of the FT-IR sample holder to record the initial FT-IR spectrum. Within certain time periods the latter procedure was repeated several times.

#### Fabric treatment

Desized, scoured, bleached 100% cotton fabric weighing  $127 \text{ g m}^{-2}$  was used throughout the investigations. The pre-weighed fabric was impregnated with a finish bath (100 mL) containing the following components: 6.98 mL TESP-SA (25.0 mmol), 2.65 g SHP (25.0 mmol), 1.80 g hydrochloric acid ( $c = 0.1 \text{ mol L}^{-1}$ ), and 40 mL EtOH. After the hydrolysis reaction of TESP-SA, SHP, dissolved in water, was added. The solution thus obtained was diluted with water to 100 mL. Subsequently, the sample ( $20 \text{ cm} \times 30 \text{ cm}$ ) was passed through a two-roll laboratory padder (HVL 500 W. Mathis AG, Niederhasli, Switzerland; air pressure: 1 bar, fabric speed:  $3 \text{ m min}^{-1}$ ). This treatment was repeated to give a wet pickup of 80–85% based on the original weight of fabric. After drying (3 min,  $80 \text{ }^\circ\text{C}$ ), the fabric was cured for a specified time at  $180 \text{ }^\circ\text{C}$  in a labdryer (LTE, W. Mathis AG, Switzerland), washed

under occasional stirring ( $1 \text{ g L}^{-1} \text{ Na}_2\text{CO}_3$ , 10 min,  $50 \text{ }^\circ\text{C}$ , 1000 mL), and finally dried again (3 min,  $80 \text{ }^\circ\text{C}$ ).

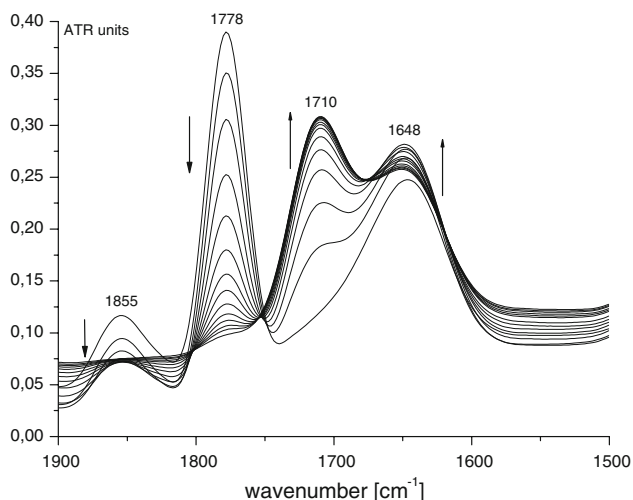
The dry crease recovery angle (DCRA) was determined according to ISO 2313 utilizing a device from Karl Schröder, Weinheim, Germany: 10 test specimens are creased and compressed under controlled conditions of time and load. After removal of the creasing load the angle formed between the two limbs is measured. The DCRA values render possible the evaluation of a crosslinking reaction between a durable press finishing agent and the cellulosic material.

## Results and discussion

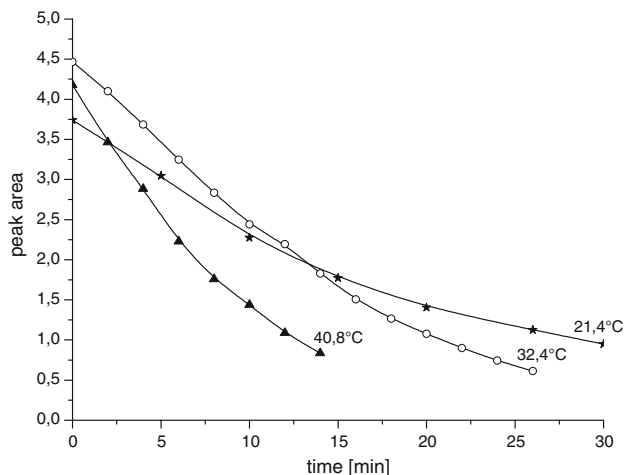
#### Hydrolysis of TESP-SA

TESP-SA was hydrolyzed using an excess of hydrochloric acid ( $c = 0.01 \text{ mol L}^{-1}$ ). The reaction was conducted at three temperatures. To evaluate the progress of the hydrolysis reaction, the FT-IR/ATR spectra were recorded at specified periods. Figure 2 shows the spectra that were obtained when TESP-SA was hydrolyzed at  $30 \text{ }^\circ\text{C}$ . The spectra were recorded every 2 min, since the spectral region between  $1900$  and  $1500 \text{ cm}^{-1}$  is of high interest. The weak absorption band at  $1855 \text{ cm}^{-1}$  is due to the symmetric stretching mode of the anhydride carbonyl groups, whereas the vibration located at  $1778 \text{ cm}^{-1}$  is assigned to the asymmetric vibration of the anhydride functionality. The intensities of these two bands clearly make evident that the anhydride group is incorporated in a cyclic system. The band at  $1710 \text{ cm}^{-1}$  is attributed to the carbonyl band of the free carboxylic acid. The absorption at  $1648 \text{ cm}^{-1}$  is due to the C–O vibration. Figure 2 shows that an increase of the reaction period results in a gradual decrease of intensity of the asymmetric stretching vibration, while the intensity of the absorption band of the carbonyl group of the free carboxylic functionality thus formed increases [15].

After the normalization of the spectra shown in Fig. 2 the peak areas were calculated and plotted against the reaction time as can be seen in Fig. 3.



**Fig. 2** Time-dependent spectra of the acid-catalyzed hydrolysis reaction of TESP-SA at 30 °C



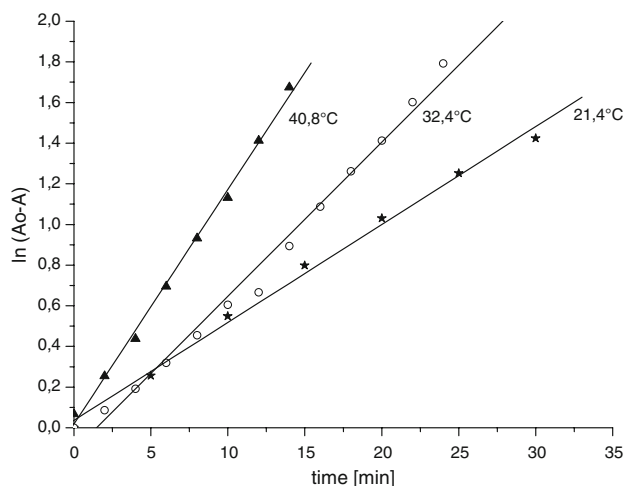
**Fig. 3** Decrease of the peak area of the anhydride band at 1778 cm<sup>-1</sup> at various temperatures

As water was used in excess, it can be assumed that the kinetic of the hydrolytic reaction obeys a pseudo-first order law. Since one component (water) is present in excess, it can be assumed that the concentration of water maintains unchanged during the reaction and therefore only the concentration of TESP-SA decreases exponentially. The reaction is pseudo-first order with respect to TESP-SA [16]. Kinetically it obeys the following relationship

$$-\frac{d[\text{TESP} - \text{SA}]}{dt} = k[\text{TESP} - \text{SA}] \quad (1)$$

Integration of this rate Eq. 1 leads to the following expression

$$\ln \frac{[\text{TESP} - \text{SA}]_0}{[\text{TESP} - \text{SA}]} = kt \quad (2)$$



**Fig. 4** Regression lines for the determination of the reaction constants for the hydrolysis reaction of TESP-SA

**Table 1** Rate constants of the hydrolysis reaction of TESP-SA at various temperatures

Temperature (°C)	Rate constant <i>k</i> (min <sup>-1</sup> )	<i>R</i>
20.4	0.04639	0.9979
32.4	0.0765	0.9963
40.8	0.1123	0.9983

[TESP-SA]<sub>0</sub> = initial concentration of TESP-SA, when *t* = 0; [TESP-SA] = concentration of TESP-SA as reaction proceeds; *k* = pseudo-first order rate constant [*t*<sup>-1</sup>].

The value of the reaction rate constant *k* can be calculated from the slope of the linear graph. Therefore we plotted ln([TESP-SA]<sub>0</sub>/[TESP-SA]) against the hydrolysis time for three temperatures. The linear regression lines of the data thus obtained are shown in Fig. 4. From the slope of the linear graphs the hydrolytic pseudo-first order rate constant was calculated which is depicted in Table 1.

The temperature dependence of the reaction rate constant follows the empirical Arrhenius equation (3).

$$k = A e^{-\frac{E_a}{RT}} \quad (3)$$

*A* = pre-exponential factor; *E<sub>a</sub>* = activation energy (mol L<sup>-1</sup>); *R* = universal gas constant = 8.314 kJ mol<sup>-1</sup> K<sup>-1</sup>.

Taking the logarithm of each side results in the following form

$$\ln k = \ln A - E_a/RT \quad (4)$$

Assuming that *A* and *E<sub>a</sub>* are independent of temperature a linear relationship is given between the logarithm of the rate constant and the reciprocal value of the absolute temperature. *E<sub>a</sub>* can be deduced from the slope of the graph and can be equated to the term *E<sub>a</sub>*/*R*, whereas *A* is

calculated from the intercept of the graph. The Arrhenius plot shows a good linear relationship with  $R = 0.99981$ .  $E_a$  is calculated as  $34.97 \text{ kJ mol}^{-1}$  and  $A$  is calculated to  $2.786 \times 10^6$  ( $32.4 \text{ }^\circ\text{C}$ ).

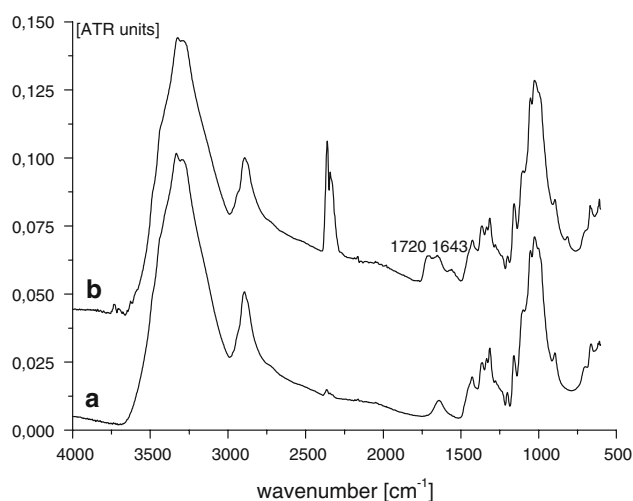
#### Application to cellulosic material

Various investigations have shown that polycarboxylic acids (PCAs) such as 1,2,3,4-butanetetracarboxylic acid (BTCA) or citric acid (CA), in combination with inorganic phosphorus-containing salts such as sodium hypophosphite  $\text{NaH}_2\text{PO}_2 \times \text{H}_2\text{O}$  (SHP) as curing catalyst, have proved to be the most effective, formaldehyde-free system to give durable press properties, such as crease resistance to cotton fabric. The reaction results in the formation of ester linkages between the hydroxyl groups of the cellulose and the carboxyl groups of the carboxylic acid thus conveying improved wrinkle resistance performance to cotton-based textile systems. Fourier transform infrared (FT-IR) spectroscopy investigations revealed that the crosslinking reaction proceeds via a cyclic five-membered anhydride intermediate [14]. Therefore we investigated the reaction of TESP-SA/SHP system with cotton fabrics. For this purpose cotton fabrics were thermally treated ( $105 \text{ }^\circ\text{C}$ : drying process,  $180 \text{ }^\circ\text{C}$ : condensation process) with various solutions containing different portions of TESP-SA (Table 2) in 25 mL. The samples were tested by means of FT-IR/ATR to determine the formation of an ester linkage and by means of DCRA measurements to test the formation of a crosslinking reaction. Figure 5 demonstrates the normalized FT-IR/ATR of the untreated cotton fabric (a), the cotton fabric that has been treated with Sol 5 at  $180 \text{ }^\circ\text{C}$  for 90 s (b). The spectrum clearly makes evident that the anhydride moiety disappeared, whereas the stretching vibration of the carbonyl function of the carboxylic group and of the ester group appears at  $1737 \text{ cm}^{-1}$  indicating the formation of the corresponding functionalities. The DCRA values reveal that no crosslinking reaction occurred since

**Table 2** Dry crease recovery angle of cotton fabrics that had been treated with different amounts of TESP-SA/SHP formulations

Solution	TESP-SA		SHP		DCRA (w + f) <sup>a</sup> ( $^\circ$ )
	(g)	(mmol)	(g)	(mmol)	
Raw material					205.0
Sol 1	2.5	8.9	0.87	8.21	188.6
Sol 2	2.5	8.9			159.2
Sol 3	5.0	17.8	1.51	16.42	208.0
Sol 4	5.0	17.8			179.4
Sol 5	10.0	35.6	3.02	32.84	212.2
Sol 6	10.0	35.6			197.8

<sup>a</sup> Warp and fill



**Fig. 5** FT-IR/ATR spectra of the raw material (a) and the TESP-SA/SHP treated cotton fabric (Sol 5) treated at  $180 \text{ }^\circ\text{C}$  for 90 s (b)

the values are even lower compared to the untreated raw material. Normally the DCRA values of a cotton fabric that has been treated with a durable press finishing agent based on polycarboxylic acids are in the region of  $280$  to  $300^\circ$  [12].

#### Conclusion

The kinetic data of the hydrolysis reaction of TESP-SA were evaluated by means of FT-IR monitoring the decrease of the asymmetric carbonyl vibration of the anhydride component. The hydrolyzed TESP-SA solution was applied to cotton material in conjunction with SHP as curing catalyst. The textile physical tests clearly demonstrated that no crosslinking reaction occurred between the cotton fibers.

**Acknowledgements** The authors are grateful to Testing Institute of the HTL Dornbirn for making available textile-physical equipment.

#### References

1. Brinker CJ, Scherer GW (1990) Sol-gel science, the physics and chemistry of sol-gel processing. Academic Press, San Diego
2. Wright JD, Sommerdijk NAJM (2001) Sol-gel materials chemistry and applications. Gordon and Breach Science Publisher, The Netherlands
3. Hench LL, West JK (1990) Chem Rev 90:33
4. Schubert U, Hüsing N, Lorenz A (1995) Chem Mater 7:2010
5. Loy DA, Baugher BM, Baugher CR, Schneider DA, Rahimian K (2000) Chem Mater 12:3624
6. Romez-Romero R, Sanchez C (2004) Functional hybrid materials. Wiley-VCH, Weinheim
7. Attia YA (ed) (1994) Sol-gel processing and applications. Plenum Press, New York

8. Mackenzie JD, Bescher EP (1998) *J Sol Gel Sci Technol* 13:371
9. Schottner G (2001) *Chem Mater* 13:3422
10. Schramm C, Rinderer B, Binder W, Tessadri R, Duelli H (2006) *Recent Res Dev Appl Polym Sci* 3:37
11. Mackenzie JD, Bescher EP (2000) *J Sol Gel Sci Technol* 19:23
12. Welch CM (1988) *Textile Res J* 58:480
13. Welch CM (1992) *Rev Prog Coloration* 22:32
14. Yang CQ, Wang X (1996) *J Polym Sci: Part A* 34:1573
15. Günzler H, Gremlich H-U (2000) *IR-Spektroskopie*. Wiley-VCH, Weinheim
16. Logan SR (1996) *Fundamentals of chemical kinetics*. Longman Group Limited, England