Silylation of OH-Polymers by Reactive Extrusion

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Summary: Silylation of poly(vinyl alcohol) and cellulose with hexamethyldisilazane (HMDS) in a twin screw extruder using ammonia as reaction medium has been studied. As the starting materials are powders which do not melt without decomposition both polymers were blended with the corresponding trimethylsilyl polymer and a reaction compartment was created using appropriate restrictor elements. Reaction profiles with temperatures below 100 °C in the reaction zone and lower temperature in the restrictor zones enabled silylation of both polymers. Residence times were as low as 15 min.

Introduction

Trimethylsilylation of cellulose and other hydroxy polymers as a way to impart solubility and melt processability has been extensively studied by us and other research groups using different silylating agents like chlorotrimethylsilane[1-3] N,O-bis(trimethylsilyl)acetamide[4, 5] or hexamethyldisilazane (HMDS)[5] and reaction media like pyridine[1,2], dimethylacetamide/LiCl[7], formamide[6], dimethylsulfoxide/paraformaldehyde[5], hexamethylphosphoric acid triamide[4, 8], or ammonia in organic solvents like tetrahydrofurane, dimethylformamide or dimethylsulfoxide and chlorotrimethylsilane[9]. Normally these reactions are heterogeneous at least in a certain range of conversion.

We studied silylation of poly(vinyl alcohol)[10] and cellulose in ammonia to combine activation of cellulose and the use of HMDS as silylating agent. HMDS gives ammonia as the only by-product. High boiling solvents or salts as formed in the case of chlorotrimethylsilane decrease the stability of silyl cellulose and require tedious purification. We achieved complete silylation of cellulose by this procedure[11] and also controlled partial silylation of cellulose with stoichiometric amounts of HMDS[12]. This indicates that the silylating agent is completely used under appropriate reaction conditions.

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Apart from the scientific interest a possible application of silylated cellulose is in the field of regeneration of cellulose after spinning or molding. Based on the chemistry involved a possible process is shown in Fig. 1. Such a process avoids the problems of huge amounts of salts, waste water and toxic reagents like carbon disulfide. Spinning and regeneration (desilylation) of cellulose are continuous steps in this process.

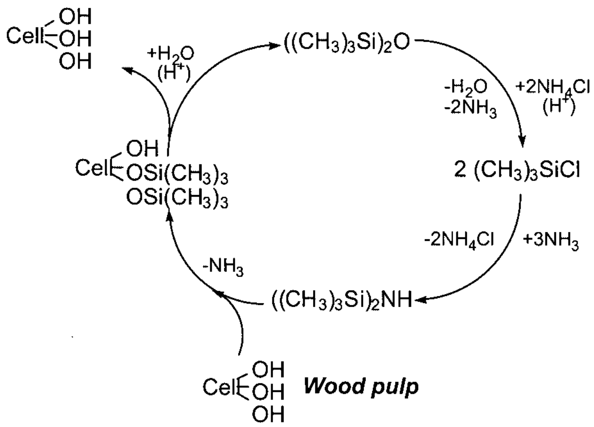


Fig. 1: Regenerated cellulose from silylation/desilylation in a closed system of reagents

Silylation in an autoclave is a batch reaction with all the inherent drawbacks. Silylation in an extruder, on the other hand, would allow for better mixing and possibly shorter reaction times.

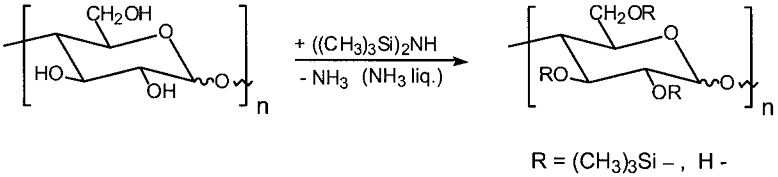
The present paper reports on our studies of the synthesis of trimethylsilyl cellulose using a twin screw extruder as reactor.

Results and Discussion

Batch silylation of cellulose in an autoclave

Details of the silylation of cellulose as shown in equation 1 and of other hydroxy group containing polymers and low molar mass compounds have been reported previously[11, 13]. Discontinuous silylations were made in stainless steel autoclaves equipped with a mechanical stirrer. Optimum conditions for complete silylation of cellulose were 4 to 14 h at 80 °C with low amounts of ammonia (1 or 2 mol per mol anhydroglucose unit) in the presence of saccharin as catalyst[11]. A study of the kinetics of this heterogeneous reaction at 80 °C was performed using saccharin as catalyst, HMDS sufficient for a DS of 1.68, and 60 mol ammonia per anhydroglucose unit (AGU). The results in Tab. 1 show that a THF soluble and an insoluble fraction was obtained in all cases. They also show that approximately 4 hours are required for complete reaction of HMDS present in the mixture.

Eq. 1:



Tab. 1: Silylation of Avicel with HMDS/ammonia in an autoclave

t / min.	THF-sol. / w.-%	DS THF-sol.	DS insol.	DS total
30	41.6	1.70	0.19	0.65
60	66.8	1.73	0.71	1.32
120	74.0	2.22	0.41	1.54
180	69.0	2.31	0.57	1.57
360	72.4	2.33	0.42	1.58

Shorter reaction times should be possible only if better mixing of the components can be achieved. Swelling of cellulose and partial reaction caused formation of a high viscous "ball" which was moved as such by the stirrer without great effect in terms of creation of new surfaces.

Silylation in an extruder

A twin-screw extruder Micro 27 (Leistritz AG Nürnberg) screw diameter 27 mm, screw length 1100 mm (40 D) was used (Fig. 2). The 10 barrel elements, each with individual heating and cooling, can be arranged as required for dosage of components, measurement of pressure, venting etc. Co-rotating and counter-rotating modes are possible with appropriate screws. Segmented screws allow arrangement of a variety of different elements at different positions for optimum performance for a given problem. In order to increase residence times the minimum screw-speed was reduced from 10 to 4 rpm.

Liquid reagents were added with constaMetric 3200 metering pumps (Thermo Separation Products, Riviera Beach FL). Torque, temperature and pressure were monitored with an Apple computer using a Terminal Panel T 21, an I/O-card ACSE 16-8 and the data treated with WorkBench Mac (Strawberry Tree, Sunnyvale CA).

Poly(vinyl alcohol), DP 500, 97.5-99.5 mol% hydrolyzed was obtained from Fluka, cellulose from Temming, Buckeye, DP 565. Silylated poly(vinyl alcohol) and cellulose (DS 2.1 or 1.3) were obtained from silylation in an autoclave. Hexamethyldisilazane (HMDS) was used as silylation agent, saccharin as catalyst.

The main problems to be solved for silylation in an extruder were

i metering of a liquefied gas (ammonia) and of HMDS in constant and small amounts

ii creation of a reaction compartment in which an ammonia pressure of up to 60 bar could be maintained "infinitely".

iii metering, transport, and mixing of an infusible powder

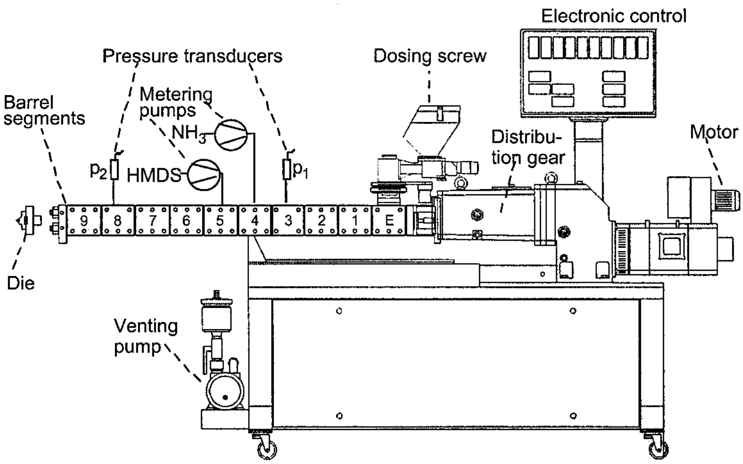


Fig. 2: Extruder used for silylation experiments (schematic)

Previous studies had shown that dried cellulose (Linters, Avicel) in an argon atmosphere takes up ammonia to an ammonia/AGU ratio of approximately 1 : 1. With increasing temperature the ammonia content continuously decreases to a ratio of only 1 : 10 at 120 °C.

Miscibility studies of ammonia and HMDS revealed complete miscibility above 24 °C and two phase behavior below this temperature [13].

CO-ROTATING SCREWS

Cellulose as a milled powder could be transported through the extruder. Kneading elements had to be used to create a closed compartment in the extruder. Addition of ammonia caused swelling which together with the kneading elements was sufficient to increase the torque above the tolerated maximum. Hence further experiments were made with counter rotating screws.

COUNTER-ROTATING SCREWS

Poly(vinyl alcohol)

Poly(vinyl alcohol) was used as a model for cellulose as it behaves similar to cellulose in many aspects (infusible powder). It has a glass transition temperature of 80 °C, silylated poly(vinyl alcohol) has a TG of 20 °C. This allowed us to find suitable parameters in particular screw geometry to create a reaction compartment in which the pressure of ammonia could be maintained. Restrictors were positioned after barrel segment 2 and in barrel segment 9 to achieve a degree of filling of 1 in these barrels, while the degree of filling was below 0.8 in the other elements. Counter-rotation slot restrictor elements were too effective for the powder as they caused automatic shut down of the extruder due to maximum torque. Replacing one of the elements by a cylindrical element improved the situation but not sufficiently.

In addition to optimizing the screw configuration a mixture of poly(vinyl alcohol) with trimethylsilylated poly(vinyl alcohol) was used as feed because this material could be premixed and pelletized in the extruder. This was also advantageous for exact feeding and reproducible degrees of filling of the barrels. The final screw configuration for this mixture is shown in Fig. 3.

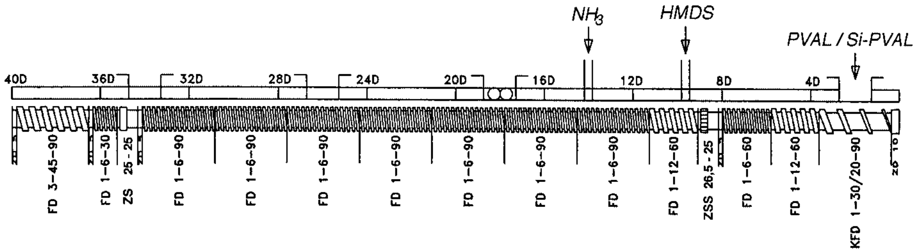


Fig. 3: Screw configuration for silylation of poly(vinyl alcohol) (counter rotating twin screw)

The temperature profile was chosen in order to have high "melt" viscosity at the confinements of the reaction zone, i.e. 60 °C for barrel elements two and three then gradual increase to 100 °C at element 5 and down to 20 °C at element 8.

The feed amounts of the different components were:

PVAL/Si-PVAL (1:1):	2,75 g/min. (31 mmol OH/min.);
Ammonia:	1,00 mL/min. (35 mmol/min.);
HMDS:	3,50 mL/min. (33 mmol Si/min.).

Screw speed was 4 rpm corresponding to a residence time of 35 min. Complete silylation was reached after 70 min. (2 residence times) and could be maintained under these conditions. The pressure in the reaction zone was in the range from 50 to 70 bar (vapor pressure of ammonia at 100 °C is 60 bar) with occasional blow offs, which, however, did not affect the degree of silylation. Due to the rather low viscosity of the ammonia containing silylated poly(vinyl alcohol) devolatilization was not possible with the venting system of the extruder.

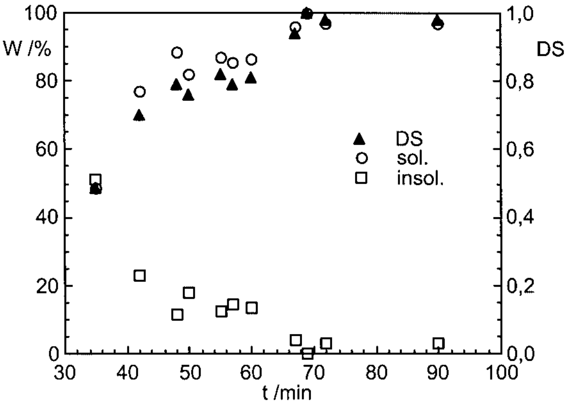


Fig. 4: DS, percentage of soluble and insoluble fractions of silylated poly(vinyl alcohol)

As with poly(vinyl alcohol) cellulose powder alone caused too high a torque. Pre-activated cellulose mixed with HMDS as lubricant worked for a short while though HMDS was pressed off in the compression zone causing again intolerable torque. Furthermore no pressure built up during ammonia addition was observed. A suitable configuration allowing for pressure built up was found using a slot restrictor element on the left screw and a cylinder of the diameter of the root of the screw (passive element) on the right screw as confinements of the reaction zone (Fig. 5).

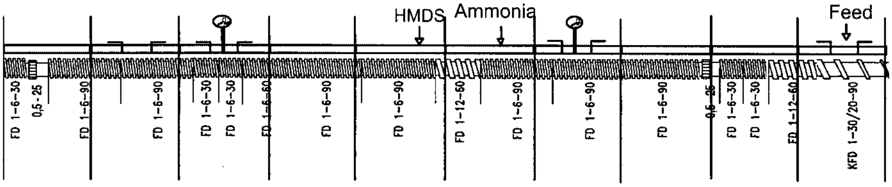


Fig. 5: Screw configuration for silylation of cellulose (counter-rotating twin screw)

For plastification cellulose was mixed with silylcellulose (4 : 1 wbw) and toluene was used as further plasticiser. HMDS could be added to the mixture outside the extruder or completely added in the extruder. A typical composition of the feed was:

Wood pulp	activated with ammonia,
silylated pulp	DS 2.3 (ratio 4 : 1),
HMDS	for DS 3,
saccharin	1 mol % rel. to OH-groups

Tab. 2: Parameters for continuous silylation of cellulose

Screw speed rpm	Output g/min.	Residence time (reaction zone) min.	DS
3.5	5	48	2.8
3.5	5	36	2.8
5	7	27	2.8
8	9	21	2.8
12	12.5	15	2.8

Optimum temperatures were 25 °C in the feed zone, which was increased to 100 °C for the third and further barrels. Residence time was between 15 and 48 min., feed was 3.5 g/min., ammonia was added 0.5 ml/min. The pressure inside the reaction zone was up to 20 bar. It was possible to reduce the temperature in the reaction zone to as low as 50 °C and still obtain a DS of 2.8.

Properties of trimethylsilyl celluloses

Silylation as well as desilylation are polymer analogous reactions which has been shown by SEC analysis of suitable derivatives[13]. Thermal properties of trimethylsilyl celluloses also depend on the degree of substitution. Soluble silyl celluloses behave like normal thermoplastic materials in dynamic mechanic thermal analysis.

Tab. 3: Thermal properties of silylated cellulose

DS	TG °C	Softening °C	TG-Onset (air) °C
1,86	224	250-260	331
1,96	201	230-240	309
2,12	195	225-235	304
2,37	200	230-240	281

They show a glass transition between 190 und 210 °C and a rubber plateau for DP 1100 which has five times the molar mass of Avicel (DP 200). Highly silylated celluloses show only a slight decrease in modulus above the glass transition. This is in agreement with the results from differential scanning calorimetry.

Conclusions

Reactive extrusion was shown to be a valuable tool for continuous silylation of poly(vinyl alcohol) and cellulose with residence times of 30 min. and less and temperatures as low as 60 °C. This is a huge improvement in comparison to the discontinuous silylation in an autoclave. The main reason for this is the better mixing achieved with the counter-rotating screws.

Acknowledgment

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