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STARCH ALKANOATES AS MODELS FOR THERMOPLASTIC POLYSACCHARIDES

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Abstract: The low degree of internal molecular mobility of stiff polysaccharide chains prevent any thermal transition in the temperature range of their chemical stability.
Substituted starches were synthesised to find the structural range, i.e. the necessary amount and length of mobile side chains which support the molecule with high enough level of internal degrees of freedom. Esterification and transesterification with hydroxy alkanoates, their polymers and lactones were used. The reaction was best catalysed with strong delocalised bases. The thermal properties of these model substances were characterised.

INTRODUCTION

Neither native starch, nor amorphous starch can be processed thermoplastically due to the limited internal mobility of the polyanhydroglucose (PAG) chain which prevents any thermal transition in the temperature range of its chemical stability. Plasticisers have to be incorporated into the starch to enable melting (Ref.1, Ref. 2). Most common plasticizers are water and glycerol, giving rise, either to physical ageing problems or to high water uptake at relative air humidities above 60%. Therefore blends of plasticised starch with polymers of limited water uptake were developed (Ref. 3). The aim of the present work was to enhance the internal mobility of the PAG chain by substitutents of high internal mobility. The selected method to prepare the model compounds was acylation of the starch.

EXPERIMENTAL PART

Materials: Native potato starch (from Blattmann, Wädenswil, Switzerland) was dried in a vacuum oven for 24h at 80°C and 0.2 mbar.
6-Hydroxycaproic acid (HCS) was prepared according to Ref. 4.

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Dimethyl sulfoxide (DMSO) (from FLUKA, puriss.; absolute; over Molecular sieve (H_2O< 0.01%); Dioxan (from Fluka, purum); ε-Caprolacton (CL) (from Fluka), Polycaprolacton (PCL) (from Union Carbide); *p*-Toluenesulfonic acid (pTSA) (from Fluka), Yttrium oxide isopropoxide ($Y_5O(OiPr)_{13}$) (from Aldrich), triethanolaminetitanate(IV) (TEAT) (from Hüls); 1,8-diazabicyclo[5.4.0]undec-7ene (DBU) (from Fluka) and the phosphazenbase: P_4-tert.Butyl (P_4) (from Fluka) were used without further purification.

Measurements: 1H-NMR spectra were recorded on a Bruker AC 300 spectrometer at 300MHz and at a temperature of 353K. Perdeuterated dimethyl sulfoxide (DMSO-d6) was used as solvent.

The heat flow calorimetry experiments were carried out with the aid of a Series 7 DSC Instrument (Perkin Elmer Corp) in pressure resistant (up to 30 bar) stainless steel capsules. Samples of approximately 20 mg were heated up, with a heating rate of 10°C/min, from –20 to 190°C. In order to evaluate the glass transition temperature (Tg) values, samples were heated to 190°C, and then they were cooled rapidly to –20°C, at a rate of 200°C/min, before being heated up again, at a rate of 10°C/min, thereby allowing Tg to be determined.

Dynamic Mechanical Thermal Analyser (DMTA) from Polymer Laboratories, Thermal Sciences Division was used from –40°C to 180°C at a heating rate of 10°C/ min in the bending modus with a frequency of 1 Hz. The Tg(1), Tg(2) and Tg(3) are the onset, inflection point, and maximum of the damping peak (Bending tan δ).

Presslings (6 mm x 30 mm x 1.5 mm) were made between 150 and 180°C at a pressure of 4 bar during 5 min.

The softening point (sp.) was used to decide about the processibility of the product. The procedure was: Pressing the sample between 2 slides at 1.5 bar at temperatures varying from 140°C to 200°C. The pressed probes were analysed with a light microscope to identify the homogeneous phase.

Preparation of substituted starch: Dry native potato starch (1 part per weight) was dissolved in DMSO (50 parts per weight) at 120°C under stirring. Residual water was distilled off under low pressure using a Soxhlet apparatus filled with molecular sieve (4Å). After 45 min. the acylating agent (2 parts per weight) and the catalyst were added subsequently. Probes were taken after the indicated time (Tab. 1, 2) and dialysed against water for 24h. The dialysed probes were extracted with dioxan to remove the unreacted acylating agent.

The determination of the degree of substitution (D.S.) was achieved by comparing the integrals in the 1H-NMR between the H(1) of the PAG-unit and the α-Hydrogens (Hα) of the substituend (Fig. 1).

RESULTS AND DISCUSSION

As acylating reagent were tested:

1 polycaprolacton with two different weight average mol mass:
PCL 1 (Mw = 250 000), PCL 2 (Mw = 10 000);

2 ε-caprolactone (CL);

3 6-hydroxycaproic acid (HCS)

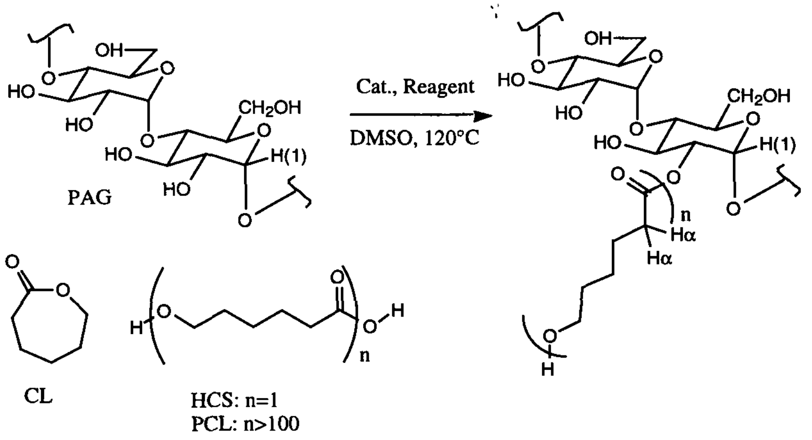
As catalyst were examined:

1 *p*-Toluenesulfonic acid (pTSA),

2 Yttrium oxide isopropoxide ($Y_5O(OiPr)_{13}$), triethanolaminetitanate(IV) (TEAT);

3 1,8-diazabicyclo[5.4.0]undec-7ene (DBU), the phosphazenbase: P_4-tert.Butyl (P_4).

Fig.1. *Reaction of starch with CL, HCS and PCL*



The results are summarised in the tables 1 and 2.

Tab. 1: *Transesterification of PCL with Starch*

Reagent	Catalyst[a] in wt.-%	Reaction time in h	Amount substituend in wt.-%[b]	sp.[c] in °C
PCl 1	$Y_5O(OiPr)_{13}$/ 5%	1	6	none
PCl 1	$Y_5O(OiPr)_{13}$/ 5%	2	11	none
PCl 1	TEAT/ 2%	1	8	none
PCl 1	TEAT/ 2%	2	15	none
PCl 1	DBU/ 10%	1.5	20	none
PCl 1	DBU/ 10%	3	25	none
PCl 1	P_4/ 5%	0.5	37	none
PCl 1	P_4/ 5%	2	41	none
PCl 1	P_4/ 10%	0.5	43	none
PCl 1	P_4/ 10%	2	50	none
PCl 1	P_4/ 10%	17	57	none
PCl 2	P_4/ 10%	0.5	13	none
PCl 2	P_4/ 10%	2	20	none

Tab. 2: *Acylation of CL and HCS with Starch*

Reagent	Catalyst[a] in wt.-%	Reaction time in h	Amount substituend in wt.-%[b]	D.S.	sp.[c] in °C
CL	$Y_5O(OiPr)_{13}$/ 5%	1	12	0.19	none
CL	$Y_5O(OiPr)_{13}$/ 5%	2	17	0.29	none
CL	DBU/ 5%	1	60	2.13	175
CL	DBU/ 5%	12	66	2.75	165
CL	P_4/ 5%	0.5	60	2.13	175
CL	P_4/ 5%	2	63	2.41	170
CL	pTSA/ 5%	1	20	0.36	none
CL	pTSA/ 5%	3	40	0.94	180
HCS	pTSA/ 5%	1	10	0.16	none

[a] The wt.-% refers to the dry starch amount.

[b] amount of the bonded reagent in the substituted starch.

[c] softening temperature

From the results of tables 1 and 2 the following conclusions can be made:

1. Up to a weight fraction of 0.57 PCL does not enhance enough the internal mobility of the PAG chains. The starch could not be processed in the thermal stability range < 200°C.
2. Starch derivatised with CL was thermoplastic.
3. The most efficient catalysts were the delocalised organic bases DBU and P_4.
4. CL reacts much faster than PCL or HCS, this is due to the enhanced reactivity of lactones compared to esters or acids.

Influence of the D.S. on the glassy solidification temperature (Tg)

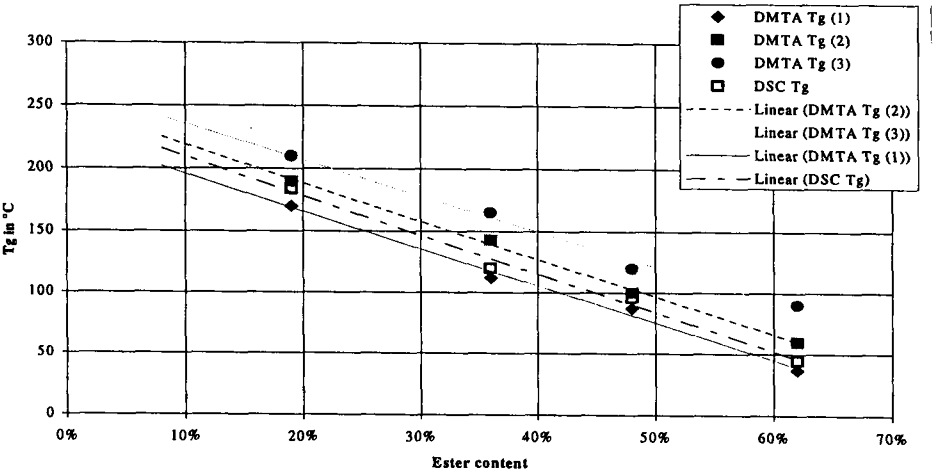
The solidification of the substituted starches was investigated with DMTA and DSC. Results on related samples are in Tab. 3 and Fig. 2.

Tab. 3 : *Estimation of the glass transition temperature (Tg).*

D.S.	**Ester content wt.-%**	**DMTA[a] in °C**			**DSC in °C**
		Tg (1)	**Tg (2)**	**Tg (3)**	**Tg**
0.12	8	none	none	none	none
0.33	19	170	190	210	184
0.80	36	112	143	165	120
1.31	48	87	100	120	96
2.32	62	37	60	90	45

[a] Tg(1), Tg(2), Tg(3): onset, inflection point, maximum of the damping peak.

Fig. 2: *Graphic of Tg vs. D.S.*



CONCLUSION

With CL derivatised starch showed at a D.S. of 0.9 a softening point at 180°C.

The thermoplasticity of the substituted starch is enhanced much significantly by introducing a high D.S. with shorter chains (CL) than by a low D.S with longer mobile side chains (PCL), keeping the wt.-% of the substituend equal.

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REFERENCES

(1) Willenbücher, R. W.; Tomka, I.; Müller R.; Carbohydrates in Industrial Synthesis; Proc. Symp. Dic. Carb. Chem. Am. Chem. Soc.; Verlag Dr A. Bartens: Berlin 1992; pp 93-111.
(2) Tomka, I.; EP 397819B1; USP 5362777.
(3) Tomka, I.; EP 596437A2.
(4) R. Huisgen, H. Ott, *Tetrahedron* **6** ,(1959), 253-267.