Carbohydrate Polymers 90 (2012) 1712–1718

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

The removal of stickies with modified starch and chitosan—Highly cationic and hydrophobic types compared with unmodified ones

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ARTICLE INFO

Article history:
Received 7 May 2012
Received in revised form 20 June 2012
Accepted 2 July 2012
Available online 27 July 2012

Keywords:
Starch
Chitosan
Stickies
Complex formation
Polycation
Hydrophobicity

ABSTRACT

The removal of dissolved and colloidal substances (DCS) in paper cycling water, so called stickies, with tailored natural polymers, having cationic as well as hydrophobic groups, was investigated using model suspensions made by the recycling of paper. The sticky content, characterized by the turbidity, the anionic charge, and the total organic carbon content (TOC) was increased by the addition of latex. The dynamic surface tension was established as useful tool for the characterization of the sticky content.

The sticky removal using the starch derivatives (with benzyl- as well as ethyl-substituents), from very low up to high cationic charge and N-(benzyl)chitosan was compared. Depending on the properties of the derivatives two possible mechanisms can be found: "charge dominated removal" or "removal dominated by hydrophobicity." It seems that turbidity and TOC are lowered especially due to charge interaction whereas the increase of the surface tension is mainly caused by the hydrophobic character of the modified natural polymers.

1. Introduction

Increasing use of de-inked pulps in combination with the closure of paper machine circuits in pulp and paper industry processes leads to an accumulation of so called trash material or tacky substances. Formation of a high amount of these substances affects paper production negatively due to lower retention of the filler or increased deposition on paper machines. Furthermore, they can also decrease the quality of the produced paper (Jidong & Yanling, 2011). These substances are brought into the process through many different sources; the recycling of paper is one of the most important.

The variety of tacky materials, present in papermaking systems, has different names: for instance, the accumulated pollutants in the water recycling system are called dissolved and colloidal substances (DCS). The composition of DCS, which mainly come from pulp, filler, recycled water, and the chemicals added during the papermaking process, is very complex. So called "stickies" are most often the result of synthetic polymers used in pressure sensitive label adhesives (Hubbe, Rojas, & Venditti, 2006). A full characterization of stickies is not easy to assess since there are many different types of stickies (Blanco & Miranda, 2007).

A lot of different characterization methods, among them mechanical methods such as the "Rotating-wire mesh-analyzer" were described (Putz & Hamann, 2003). It was used in order to quantify the efficiency of different fixing agents (Putz, Hamann, & Gruber, 2003). Otherwise, physico-chemical methods such as measuring the cationic demand, the zeta-potential or the turbidity of wastewater were applied (Gao, Qin, & Li, 2011) showed that the addition of cationic talc can effectively decrease the content of stickies and DCS by reducing the cationic demand of the pulp and the turbidity of the filtrate (Gao et al., 2011). Unfortunately, none of the sticky test methods investigated was found to be universally applicable, i.e., suitable for all types of stickies. Therefore, the most suitable method must be chosen for each particular case and problem area (Putz & Hamann, 2003).

Previous articles or reviews such as Hubbe et al. (2006) and Glazer (1991) have considered the origin, the nature, as well as the removal of the DCS. The variety of chemical additives, which were used in paper industry to combat deposit problems, is described. Among them are organic polymers with huge ranges of molecular mass, charge, and water loving vs. sparingly soluble character. The effects of these polymers are greatly dependent on how these materials interact with surfaces (Hubbe et al., 2006). Important

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http://dx.doi.org/10.1016/j.carbpol.2012.07.055

classes of polymers are cationic polymers with very high mass, e.g., polyacrylamides (well known as retention aids) or high charge cationic polymers (Richardson, 1995; Strauß & Großmann, 1997). Surfactants, hydrophilic polymers of intermediate mass are applied as well as polyelectrolytes with partially hydrophobic character. It was shown that the adsorption tendency of polyelectrolytes (PEL) onto tacky materials can be increased by derivatization with hydrophobic substituent groups. Various copolymers of cationic, hydrophilic, and hydrophobic monomers are promising detackifying agents for resinous material (Fink, 1993; Juzukonis & Chen, 2000).

Tailor-made cationic polymers are very effective for fixing interfering substances, because they reduce the tendency of adhesive, hydrophobic substances to agglomerate and slow down the rate at which secondary stickies are formed (Meixner, Auhorn, & Gercke, 1998). They are able to demonstrate; that for an efficient sticky removal not only the cationic charge is necessary, but also the hydrophobicity. Whether or not a certain polymer is effective depends on the type of detrimental substances.

Only a few papers describe the application of starch, modified starch, or other carbohydrate polymers as flocculants for sticky removal (Glittenberg, Hemmes, & Bergh, 1993; Huo, Venditti, & Chang, 2001; Knubb & Zetter, 2002; Luo & Wang, 2010). The role of charge on the destabilization of micro-stickies was investigated by comparing the strong polycation polydiallyldimethyl-ammoniumchloride (PDADMAC) with commercial cationic starch. The agglomeration of micro stickies with PDADMAC occurred mainly via a charge neutralization mechanism. In contrast, the agglomeration of micro-stickies with cationic starch “had a more complicated behavior” (Huo et al., 2001).

Highly cationic starches (HCS) with different branching degrees and molecular weights were investigated by their influence on the dissolved and colloidal substances (DCS) controlling effects using zeta-potential, cationic demand, drainage speed, and turbidity. The study indicated that the degraded linear HCS had better performance in controlling micro-stickies than the branched HCS (Luo & Wang, 2010).

The interactions of trash with combinations of polyelectrolytes such as PDADMAC (as trash catcher) and cationic starch (as dry strength agent) were studied by Glittenberg et al. (1993).

Our own investigations described recently the interaction between modified starch and model extracts of recycled domestic newspaper and sticky material (Petzold, Schönberger, & Schwarz, 2011). The surface tension measurement was established as a useful tool to characterize the surface activity and therefore the sticky content of the suspension (Petzold, Schönberger, Genest, & Schwarz, 2012). The prepared sticky containing model suspension was highly surface active. On this basis the interaction of 3 modified starches with the same “medium” cationic charge, but different hydrophobicity, was investigated with the model suspension. The interaction and complex formation which leads to precipitation, decreasing of turbidity and TOC, but increasing of the surface tension were confirmed. The most important consequence of this work was that the amount of cationic charge is essential for sticky removal, but the result can be improved by a higher degree of hydrophobicity.

In the present paper, new types of cationic starch with hydrophobic groups, namely benzyl- as well as ethyl-substituents, from very low up to high content of cationic groups were described. The dependence of the sticky removal on the properties of the starch derivatives, especially on cationic charge and hydrophobic character were investigated and compared with N-(benzyl)chitosan. In contrast to Petzold et al. (2011) the bubble pressure method, a relative simple and time-saving test method was used for the dynamic surface tension measurement.

Table 1
Properties of the sticky containing suspensions (SCS).

Suspension wastewater	Charge [mmol/l][a]	Turbidity [NTU]	TOC [mgC/l]
Extrakt of domestic newsprint	−0.22	1.9	77.9
Extrakt 1 + post it	−0.22	2.6	125
Extrakt 1 + post it + latex	−1.67	5956	>4080

[a] Determined as “cationic demand” by polyelectrolyte titration.

2. Experimental part

2.1. Material

The water used in the present study was filtered via a Milli-Q Advantage A10 (18.2 mΩ cm at 25 °C).

The starch sample used was potato starch provided by CHP Carbohydrate Pirna GmbH & Co. KG, D-01796 Pirna, Germany. Chitosan with a deacetylation content of 85% was provided by BioLog Biotechnologie und Logistik GmbH, D-06188 Lands-berg, Germany. Benzyl chloride (BnCl, Aldrich) and 2,3-epoxypropyltrimethylammonium chloride as 70% aqueous solutions (EPTMA, Aldrich) were used without further purification. The other chemicals were also used as received.

2.2. Sticky containing model suspensions

Sticky containing wastewater was prepared by cooking 10 g of comminuted newspaper in 1 l of tap water for 4 h under stirring. Then the pulp was de-inked (by the removal of the top layer). The remaining suspension had two phases: the solid material (fibers) on the bottom and a liquid phase with low turbidity above. This liquid was separated and characterized as described below. Because the surface activity (and therefore the content of detrimental substances of this suspension is not very high, the sticky content was increased by the addition of 0.8 g of so called post-it’s and 10 ml of styrene–butadiene latex (which is used in coatings)) for 1 l extract. As shown in Table 1, the addition of post-it’s does not influence the charge. But the addition of latex significantly decreases the negative charge and increases the turbidity as well as the total organic carbon content (TOC). This extract with a surface tension of 59.4 mN/m (measured with the bubble pressure tensiometer) was used to investigate the interaction with starch.

2.3. Modification of natural polymers

The properties of the modified natural polymers are summarized in Table 2.

The modification of starch respectively chitosan was performed as described in Sections 2.3.1–2.3.3. Afterwards the tailored products were dissolved in Millipore water (1 g/l) under stirring.

2.3.1. Synthesis of benzylhydroxypropyltrimethylammoniumstarch chloride (BnHPMAS)

The benzylated cationic potato starch derivatives (benzyl 2-hydroxy-3-trimethylammoniumpropyl (HPMA) starch chloride), with substitution degrees (DS) from 0.25 to 0.58 of benzyl moieties, and a molar degree of substitution (MS) from 0.35 to 0.88 of cationic groups were synthesized according to the routes described elsewhere (Heinze, Rensing, & Koschella, 2007). Briefly in a typical procedure, 500 g starch (15% water content corresponding to 425 g dry material, 2.62 mol) were suspended in 1 l saturated aqueous Na_2SO_4 solution and activated with 185 ml 11 M aqueous NaOH (2 mol, 0.9 mol/mol anhydroglucose unit, AGU) for 1 h at 60 °C. After addition of 185 ml benzyl chloride (203.5 g, 1.6 mol, 0.6 mol/mol AGU), the mixture was stirred for 6 h and cooled down to room

Table 2
Molar degree of substitution (MS_N) of the cationic hydroxypropyltrimethylammonium moieties (HPMA), degree of substitution of the hydrophobic functions (DS_{Bn} or DS_{Et}), and charge of aqueous solutions (1 g/l) of unmodified starch, benzylhydroxypropyltrimethylammonium starch chlorides (BnHPMAS), ethylhydroxypropyltrimethylammoniumstarch chlorides (EtHPMAS) as well as N-(benzyl)chitosan.

Polymer	Type	MS_N [a]	DS_{Bn} [b]	DS_{Et} [c]	Charge[d] (mmol/l)
A	Starch unmodified	–	–	–	0
B	BnHPMAS	0.67	0.50	–	2.49
C	BnHPMAS	0.35	0.25	–	1.79
D	BnHPMAS	0.67	0.25	–	2.44
E	BnHPMAS	0.88	0.25	–	2.72
F	N-(benzyl)chitosan	1.00	0.50	–	4.76
G	EtHPMAS	0.04	–	0.09	0.17
H	EtHPMAS	0.10	–	0.09	0.16
I	EtHPMAS	0.32	–	0.09	0.25
J	EtHPMAS	0.04	–	0.47	0.13
K	EtHPMAS	0.08	–	0.47	0.22
L	EtHPMAS	0.36	–	0.47	0.22
M	EtHPMAS	0.03		0.24	−0.15
N	EtHPMAS	0.03		0.39	0.14

[a] Molar degree of substitution with hydroxypropyltrimethylammonium chloride groups.
[b] Degree of substitution with benzyl moieties.
[c] Degree of substitution with ethyl groups.
[d] Polyelectrolyte titration.

temperature. The product was filtered off using a sintered glass filter (pore size G3), suspended in water and neutralized with HCl. The benzyl starch was washed with water free of Na_2SO_4 (tested with $BaCl_2$), twice with methanol, and dried in vacuum at 60 °C. DS_{Bn} 0.25.

The benzyl starch (DS_{Bn} 0.25, 20 g, 0.11 mol) was suspended in 80 ml 60% 2-propanol (v/v) and activated with 2 ml 11 M aqueous NaOH for 1 h at 60 °C. After the addition of 20 ml (0.11 mol, 1 mol/mol modified AGU) EPTMA (70% in water) and further stirring for 6 h at 60 °C, the mixture was cooled to room temperature and the product was neutralized with HCl. It was washed three times with 2-propanol, dissolved in water, and precipitated in 2-propanol. The procedure was repeated three times. The product was dried in vacuum at 40 °C. (Polymer **C** (Fig. 1); DS_{Bn} 0.25, MS_N 0.35 as an example).

The DS_{Bn} was calculated by the integration of the peaks in the ^1H NMR spectra of perpropionylated benzyl starch samples according to Heinze et al. (2007). The MS_N were determined by nitrogen elemental analysis as described (Heinze et al., 2007).

2.3.2. Synthesis of ethylhydroxypropyltrimethylammoniumstarch chloride (EtHPMAS)

In a typical procedure, 100 g dry starch (0.61 mol) were dissolved in 1000 ml of a DMSO/water mixture (2:3), subsequently activated with 120 ml 8 M aqueous NaOH and stirred for 2 h at 20 °C. After addition of 110 g gaseous ethylchloride, the mixture was stirred for 8 h and cooled down to room temperature. The product was separated by filtration using a glass filter (pore size 4), subsequent suspension in water and neutralization with 30% aqueous acetic acid solution. The ethyl starch was washed once with methanol, twice with acetone and dried in vacuum at 50 °C. DS_{Et} 0.47.

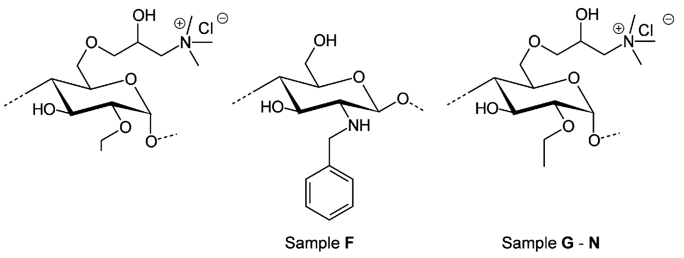

Fig. 1. Structures of modified natural polymers.

The ethyl starch (DS_{Et} 0.47, 15 g) was suspended in 200 ml 40% aqueous 2-propanol and activated with 8 ml 6% aqueous NaOH for 2 h at 50 °C. After addition of 35 ml 50% aqueous EPTMA and stirring for 10 h at 50 °C, the mixture was cooled to room temperature and neutralized with acetic acid. It was washed two times with acetone. The product was dried in vacuum at 30 °C. (DS_{ET} 0.47, MS_{HPTMA} 0.36, polymer L, Table 2 as an example).

The DS_{Et} was calculated by the integration of the peaks in the ^1H NMR spectra of peracylated ethyl starch. The MS_{HPTMA} was determined by nitrogen elemental analysis.

2.3.3. N-(benzyl)chitosan

The benzylation of chitosan was carried out according to Rabea, Badawy, Steurbaut, and Stevens (2009). Briefly, 3 g chitosan (18.6 mmol) were dissolved in 300 ml 1% (v/v) aqueous acetic acid solutions. A solution of benzaldehyde (1.58 g, 14.8 mmol) in 10 ml methanol was added drop by drop. The mixture was allowed to react for 1 h at room temperature under stirring. Then, the pH was adjusted to 4.5 by adding 1 M aqueous NaOH and a solution of 1.05 g sodium cyano borohydride (27.9 mmol, 1.5 mol/mol aldehyde) in 10 ml water was added. The mixture was stirred 1.5 h at room temperature. By addition of 1 M aqueous NaOH, the pH was adjusted to 10. The precipitate of the N-(benzyl)chitosan was filtered off and washed three times with water. The unreacted aldehyde was separated by extraction of the crude product with ethanol/diethylether (1:1, v/v) in a soxhlet for 2 days. The product was dried in vacuum at 40 °C. (Polymer **F** (Fig. 1). DS_{Bn} 0.50 as an example).

The DS_{Bn} was calculated by the integration of the peaks in the ^1H NMR spectra of peracetylated benzyl chitosan according to Eq. (1):

$$DS_{Bn} = \frac{1}{5}\frac{I_{\text{Bn-Aromat}}}{(3I_{\text{Bn-Aromat}} + 5I_{\text{Ac}})/45} \qquad (1)$$

2.4. Interaction between the model suspension and starch A, benzylhydroxypropyltrimethylammoniumstarch chlorides (HPMAS, *B*–*E*), N-(benzyl)chitosan (*F*), ethylhydroxypropyltrimethylammoniumstarch chlorides (EtHPMAS, *G*–*N*)

Increasing quantities (0.5; 1; 5; and 10 ml of different polysaccharide derivative solutions (1 g/l) in water) were added to 50 ml of the model suspension under stirring. The total volume of the mixture was kept constant (100 ml). So, the amount added is between 5 and 100 mg of polymer derivative per 1 l of the highly anionic and surface active sticky containing model suspension.

2.5. Characterization methods

2.5.1. Polysaccharides and their mixtures

The polyelectrolyte titration (PCD T3, MÜTEK, Germany) was used to determine the charge of starch **A**, BnHPMAS (**B**–**E**), EtHPMAS (**G**–**N**), and N-(benzylchitosan) **F** as well as the charge of the mixtures between the sample and the sticky containing model suspension with the streaming current detector.

In addition, the turbidity of the mixtures was measured with Turbidimeter 2100 (Hach, Germany) and the TOC (total organic carbon) with a TOC Analyzer of Shimadzu. The dynamic surface tension of the mixture was characterized with the bubble pressure tensiometer (SITA Messtechnik, Dresden, Germany) at 22 °C. The small yet precise tensiometer for use in and outside of laboratories covers applications with focus on very dynamic to semi-static surface tension and allows us to characterize a large amount of samples in relative short time. The maximum bubble lifetime was 60 s in all experiments.

2.5.2. Characterization of model suspensions

Model suspensions were characterized using the same methods as described in Section 2.5.1. As already shown in Table 1, the pulp obtained by the simulated recycling procedure of domestic newsprint has a low turbidity and a relative low TOC-content. The surface tension, which is lower than that of water (<72 mN/m) demonstrates, that the suspension is surface active. But the other parameters show that the sticky content is low. The addition of so called post-it's (line 2 in Table 1) does not really influence the charge or the turbidity, but lowered the surface tension. The surface activity was further increased by the addition of anionic styrene–butadien latex. This model suspension (line 3 in Table 1) with high anionic charge, high turbidity, and TOC and low surface tension (59.4 mN/m) was selected to study the interaction with different types of functionalized starch.

3. Results and discussion

3.1. Properties of the products

The starch products **B**–**E** and **G**–**N** substituted with hydrophobic groups as well as cationic functions covered a wide range of properties. Natural, unmodified starch as well as cationic hydroxypropyltrimethylammonium chloride (HPMA) ether of ethyl- or benzyl starch were investigated. The degree of substitution of cationic functions (MS_N) was varied in the range between 0.03 and 0.88 (starch **E**). Therefore, the influence of increasing cationic content at constant hydrophobicity, or the influence of the same MS_N at different DS_{Bn} (benzyl) or DS_{Et} (ethyl moieties) can be compared. The cationic charge was measured at the pH, which was obtained during solution preparation. N-(benzyl)chitosan **F** was poorly soluble at neutral pH. Therefore some drops of acetic acid were added. For all samples the measured cationic charge increased with increasing MS_N, but was not proportional.

The water solubility of the ethyl-starches decreases significantly with increasing DS.

3.2. Interaction between the different natural polymers and the sticky-containing suspension

In the following, natural (unmodified) potato starch will be compared with modified starches with cationic and/or hydrophobic functionalities.

For comparison, the interaction between natural (unmodified) potato starch and the sticky-containing suspension was investigated and it was clearly shown that the addition of unmodified starch did not have any influence on sticky removal: neither for decreasing the turbidity or the total organic carbon (TOC) content, nor for the reduction of the surface activity. That means, that the stickies are unaffected by the addition of unmodified starch.

In contrast, the interaction between functionalized starches and DCS and therefore the sticky removal is significantly influenced by the main properties of the modified starches: cationic charge and hydrophobicity.

At first, 3 types of benzylhydroxypropyltrimethylammonium starch chlorides (BnHPMAS) with the same hydrophobicity and increasing cationic charge (starch **C**–**E**) will be compared with BnHPMAS **B**, which has the same charge as polymer **D** (see Table 2). The cationic charge of all these products is comparable. It is lower than that of some synthetic polycations such as polydiallyldimethyl-ammoniumchloride (PDADMAC), but higher as the charge of products **G**–**N**, which will be described later (Table 2). As shown in Fig. 2, the anionic charge of the sticky containing suspension (SCS) decreases with increasing amount of cationic starch. That means, the systems tends to become neutral. However, the cationic charge (or the amount of starch added) is too low for total neutralization. The differences between products **B**–**E** are small.

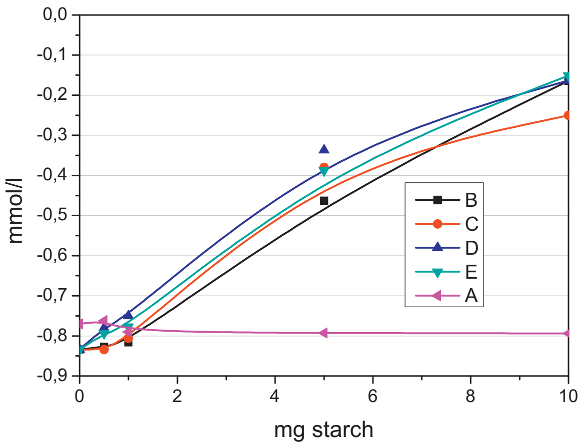

Fig. 2. Anionic charge of sticky containing suspension, mixed with starch A or benzylhydroxy-propyltrimethylammoniumstarch chloride (BnHPMAS **B**–**E**) in dependence on the added amount (MS_N and DS_{Bn} values compare Table 2).

In contrast, the addition of unmodified starch does not influence the negative charge of the suspension. Due to the interaction between the SCS and BnHPMAS, a formation of polyelectrolyte complexes and their precipitation occurs (Petzold et al., 2011), followed by a significant reduction of the turbidity and the TOC. Interestingly, the decrease of the turbidity is nearly proportional to the decrease of the TOC. This is shown for BnHPMAS **B** as an example in Fig. 3 and also summarized in Table 3. Very low values for turbidity and TOC are obtained at the highest dosage of samples **B–E**, where the charge of the mixture is near the neutrality (see Fig. 2).

However, the application of unmodified starch does neither reduce the turbidity or the TOC, nor increase the surface tension.

As described recently (Petzold et al., 2011), at optimum BnHPMAS dosage the surface tension of the mixture increased as a result of the interaction between SCS and the starch derivatives and their complex formation. This confirmed that the stickies were removed and the surface activity in the system became lower. Between three types of BnHPMAS with the same, medium cationic charge,

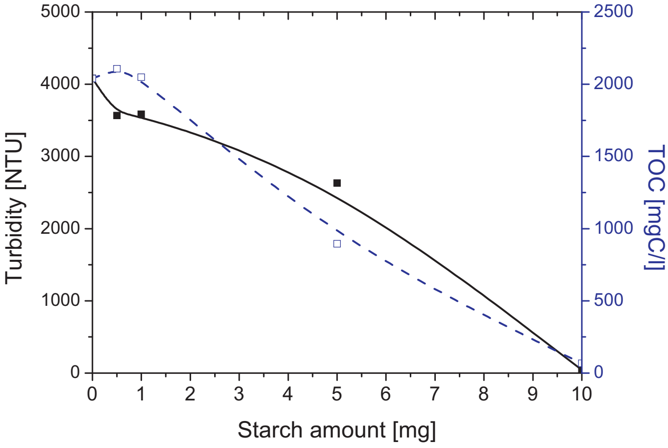

Fig. 3. Sticky containing suspension in presence of benzylhydroxy-propyltrimethylammoniumstarch chloride **B** (DS_{Bn} 0.50, MS_N 0.67); Turbidity and TOC (dotted line) in dependence on the amount of sample **B** added.

Table 3
Interaction between the model suspension and benzylhydroxypropyl-trimethylammoniumstarch chlorides (BnHPMAS), ethylhydroxypropyltrimethyl-ammoniumstarch chlorides (EtHPMAS), and N-(benzyl)chitosan: properties of the obtained mixtures in dependence on the added polymer amount; excellent results (Turbidity values < 100 NTU or TOC < 100 mgC/l and surface tensions > 65 mN/m) are printed in bold.

Polymer[a]	Amount added	Potential/charge		Turbidity	Surface tension[b]	TOC
	mg	mV	mmol/l	NTU	mN/m	mgC/l
B	0.5	−609	−0.83	3568	64.4	2108
BnHPMAS	1.0	−479	−0.82	3585	64.1	2048
	5.0	−442	−0.42	2632	63.3	896.4
	10.0	−319	−0.16	**44**	**65.4**	**67.4**
D	0.5	−536	−0.78	4901	64	2151
BnHPMAS	1.0	−538	−0.75	5351	63.5	2109
	5.0	−455	−0.34	927	62.9	358.7
	10.0	−342	−0.16	**75.5**	62.6	**67.1**
F	0.5	−498	−0.63	3512	63.3	1443
N-(benzyl)chitosan	1.0	−316	−0.38	3860	63.1	1060
	5.0	155	0.05	**89.3**	**68.7**	193
	10.0	302	0.21	3050	**67.1**	1020
I	0.5	−558	−0.85	3474	**68.6**	940.9
EtHPMAS	1.0	−602	−0.83	3509	**68.6**	783.2
	5.0	−519	−0.84	3427	**68.5**	1356
	10.0	−541	−0.36	**51.2**	**69.6**	**48.84**
J	0.5	−500	−0.79	3900	**68.1**	1551
EtHPMAS	1.0	−541	−0.76	4605	**67.2**	1528
	5.0	−482	−0.38	2790	**67.1**	219.5
	10.0	−449	−0.38	137	**66.7**	128.1
L	0.5	−506	−0.86	3960	64.3	911.8
EtHPMAS	1.0	−602	−0.86	4620	64.2	1449
	5.0	−509	−0.46	1885	**65.1**	234.1
	10.0	−503	−0.42	340	**65.1**	**56.37**
N	0.5	−451	−0.73	3904	**66.7**	1828
EtHPMAS	1.0	−376	−0.71	4626	**67.3**	1608
	5.0	−485	−0.43	1474	**67.1**	236
	10.0	−509	−0.35	273	**67.7**	1183
Model-suspension	–	−604	−1.67	5956	59.4	4083

[a] Molar degree of substitution of HMPA, degree of substitution of Bn and Et see Table 2.

[b] Characterized with bubble pressure method; surface tension, obtained at $t = 60$ s.

most effective removal was found for the product with the highest hydrophobicity.

For the samples **B**–**E** a moderate increase of the surface tension with increasing amount of product was measured. As an example, the dynamic surface tension of the mixture is shown in dependence on the addition of BnHPMAS **B** (Fig. 4). Generally, the surface tension of the pure extract decreases with time and the equilibrium surface tension was reached after longer time (up to 20 min) because the surface active (hydrophobic) components need some time to move to the surface. A similar behavior can be found for the mixtures between extract and BnHPMAS. The surface tension of all samples decreases with time, due to the hydrophobic character of the mixture and the formation of surface active complexes. The bubble pressure tensiometer allows to measure up to 60 s, where the equilibrium surface tension is not reached, but the surface tension increases step by step up to 65.6 mN/m with increasing amount of BnHPMAS **B**. This confirms that the stickies are removed by the interaction between the SCS and BnHPMAS and precipitation.

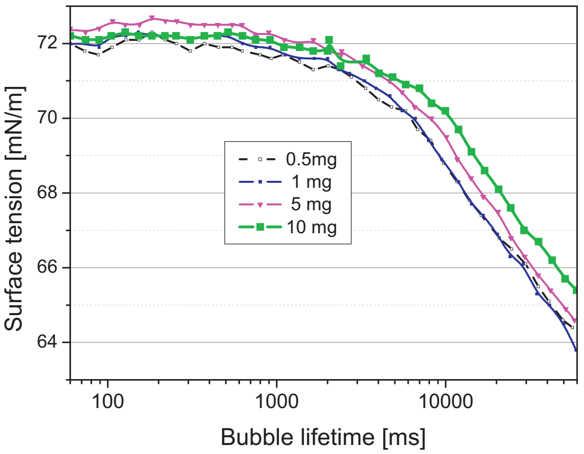

Fig. 4. Dynamic surface tension of mixtures between the SCS and increasing amount of benzylhydroxypropyltrimethylammoniumstarch chloride **B** (DS_{Bn} 0.50, MS_N 0.67).

In Fig. 5 the influence of BnHPMAS with similar properties on the surface tension is compared. BnHPMAS **B**, which has the highest hydrophobicity, is very effective at high polymer concentration. Among the types **C**–**E**, which have the same hydrophobicity ($DS_{Bn} = 0.25$), the highest surface tension can be found for sample **E** with the highest cationic charge (see Table 2).

N-(benzyl) chitosan **F** (DS_{Bn} 0.50), has a higher degree of cationic substitution than BnHPMAS **B**–**D**, because it contains amino groups in every repeating unit. This was also confirmed by polyelectrolyte titration. As a result, neutralization of the SCS is obtained with a lower amount of polymer **F**. At an amount of 5 mg, the lowest TOC, the lowest turbidity and the highest surface tension were found. The surface tension increased up to 68.7 mN/m. In contrast to the systems which were described above, the charge of the mixture with 10 mg of N-(benzyl) chitosan (polymer **F**) becomes positive, but the sticky removal is efficient with 5 g, were the mixture is

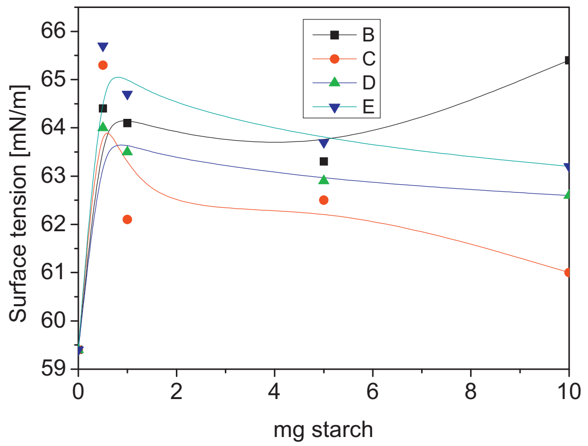

Fig. 5. Surface tension of mixtures between the sticky containing suspension and different benzylhydroxypropyltrimethylammoniumstarch chloride (BnHPMAS **B**–**E**, MS_N and DS_{Bn}) values compare Table 2 in dependence on the amount added.

neutral. The decrease of turbidity and TOC in dependence on the amount of polymer **F** is shown in Fig. 6.

The fact, that synthetic charged polymers are effective at an optimum polymer dosage, is well known from flocculation of inorganic particles (Petzold & Schwarz, 2006). Only in a certain dosage range, which depends on the charge of the suspension, the turbidity can be removed effectively. This optimum is called “flocculation window” and for an effective use in the industry, the flocculation window should be broad. It is also known that highly cationic polymers can effectively decrease the turbidity only at a certain dosage (small flocculation window), because the turbidity is increased by the particle restabilization, due to the charge reversal (Petzold, Goltzsche, Mende, Schwarz, & Jäger, 2009). Carbohydrate polymers with high cationic charge, such as N-(benzyl) chitosan (**F**) have the same behavior as shown in Fig. 6. The next group of functionalized starches (EtHPMAS **G**–**N**) has cationic charge and hydrophobic moieties due to the modification described in Section 2.3.2. But compared with BnHPMAS **B**–**E** and N-(benzyl) chitosan **F**, the detected charge of **G**–**N** is only 10% of the products described above. So the effect on sticky removal should be different. At first, as expected, the amount of cationic charge of **G**–**N** is too low for the neutralization of the suspension. Therefore only a moderate reduction of TOC and turbidity was obtained. Nevertheless, as found for BnHPMAS **B**–**E**, the TOC and turbidity decrease with increasing amount of EtHPMAS. But the minimum values, obtained with EtHPMAS **K** (turbidity: 143 NTU, TOC: 207 mg C/l; see Fig. 7), are higher than with BnHPMAS **B** (Fig. 3) and so it seems that polymers with lower charge are not as effective in decreasing the turbidity.

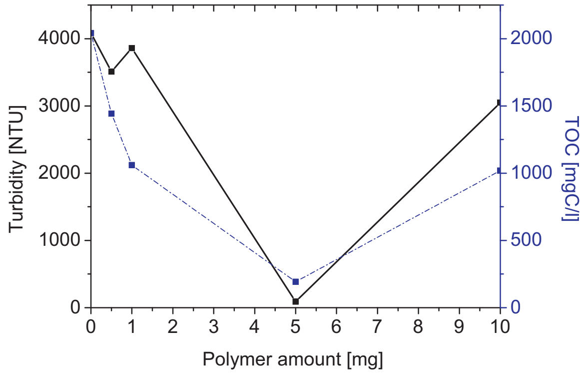

Fig. 6. Sticky containing suspension in presence of N-(benzyl)chitosan (polymer **F**, DS_{Bn} 0.50); turbidity and TOC (dotted line) in dependence on the amount of polymer added.

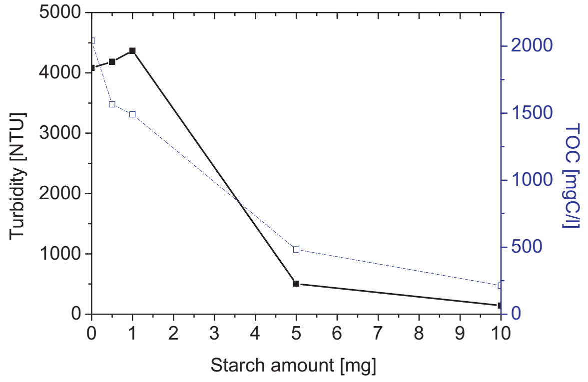

Fig. 7. Sticky containing suspension in presence of ethylhydroxypropyltrimethylammoniumstarch chlorides **K** (DS_{Et} 0.47, MS_N 0.08); turbidity and TOC (dotted line) in dependence on the amount of polymer added.

In contrast, an increase of the surface tension, compared with the “pure” SCS, and also with BnHPMAS **B** can be noticed. Whereas the surface tension is between 64 and 66 mN/m with **B**, this value is about 68 mN/m with EtHPMAS **K** (Fig. 8).

However, in contrast to the results obtained with BnHPMAS **B**–**E** (see Fig. 4 as an example), the surface tension is nearly independent of the amount of EtHPMAS **K** added. The smallest amount of **K** has the same effect on surface tension as the highest. That means the removal of one part of the “sticky-components” does not necessarily need a high cationic charge. A small increase of the cationic charge with EtHPMAS **L** (DS_{Et} 0.47, MS_N 0.36) compared with EtHPMAS **J** (DS_{Et} 0.47, MS_N 0.04) does further increase the surface tension (max. 69.55 mN/m). A sample with low cationic charge combined with low hydrophobicity (**H**, DS_{Et} 0.09, MS_N 0.10) can remove one part of the stickies (increase of the surface tension), but can only slightly reduce the turbidity or TOC.

EtHPMAS **M** and **N**, which have the lowest molar degree of substitution of cationic functions of the starch derivatives studied ($MS_N = 0.03$) are not able to reduce the turbidity and TOC, respectively (Table 3). A small increase of the surface tension can be noticed (up to about 67 mN/m). A summary of important details and the results, which were obtained with BnHPMAS and EtHPMAS is given in Table 3. The selected samples allow comparing, the influence of benzyl- vs. ethyl-groups containing polymers,

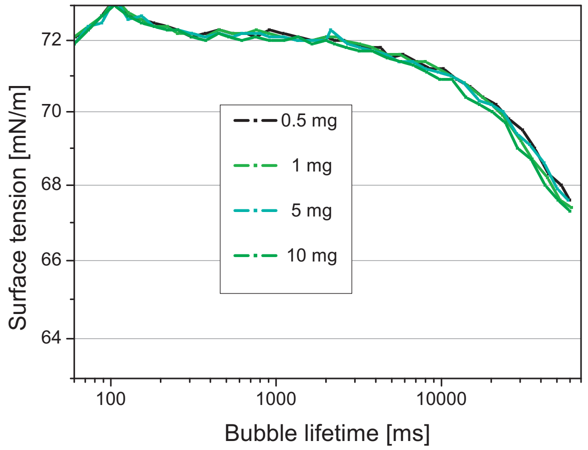

Fig. 8. Dynamic surface tension of mixtures between the SCS and increasing amount of ethyl-hydroxypropyltrimethylammoniumstarch chlorides **K** (DS_{Et} 0.47, MS_N 0.08).

the degree of hydrophobicity or the behavior of modified chitosan. By comparing different properties such as the charge of the suspension, their turbidity, TOC or surface tension, some information on the flocculation mechanism is given.

By comparing the results summarized in Table 3, it can be assumed that the sticky-containing model must have two different components: one part which can be removed by charge interaction and one which is removed due to hydrophobicity. For instance, polymers without, or with low cationic charge are not able to reduce the turbidity or TOC significantly, but they are able to increase the surface tension. In contrast, the turbidity or TOC can be dramatically reduced by the application of an optimum amount of cationic charge.

The situation is very complex. It depends on the "equilibrium" of starch properties which of the two mechanisms is effective: "charge dominated removal" or "removal, dominated by hydrophobicity." Therefore, such types of starch which are moderate cationic and also hydrophobic are most effective, such as **B** and **I**.

4. Conclusions

SCS containing model suspensions were created by cooking of small cutted fragments of newspaper and the addition of latex. They were characterized by different methods such as polyelectrolyte titration, measuring the turbidity or TOC. As already discussed (Blanco & Miranda, 2007), cationic demand only predicts a certain type of stickies, therefore full characterization of stickies is necessary.

It was proved that the dynamic surface tension of the suspension is one important tool to characterize the sticky content and can give information on the interfacial properties of the mixture. As an example, the model suspension which is made only from paper has a lower surface activity (or higher surface tension) than such model systems, which are enriched with stickies (due to the addition of post-it's or latex).

It was shown that the new tailored starch products having cationic charge as well as hydrophobicity are able to remove different types of stickies by different mechanisms. The type of interaction between SCS and starch derivatives depends on the properties of natural based polymers. Polymers **B**–**F** with "higher" cationic charge (benzyl starch, chitosan, or synthetic polycations) interact via the charge neutralization mechanism and an optimum dosage is important. Polymers with low charge, but hydrophobic moieties (EtHPMAS) can remove the stickies due to hydrophobic interactions. For instance, the addition of polymer **I** to the model suspension leads to a significant increase of the surface tension (about 69 mN/m compared with 59.4 mN/m for the model). But, in contrast to the polymers with higher charge, the influence of polymer dosage on the surface tension is minor.

Acknowledgments

The support from Bundesministerium für Wirtschaft und Arbeit (BMWA)/Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AiF-Nr. 15875) is gratefully acknowledged.

Anja Caspari is thanked for her help with TOC-determination and Sven Frenzel is thanked for his experimental work. The authors thank Manuella Kötteritzsch for her technical assistance by the preparation of the starch derivatives.

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