



Session: Modeling and Simulation



Identification of Thermal Degradation Process of Starch in Production of Environmentally Friendly Flocculants

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ABSTRACT

Chemical modification of starch can be used to produce environmentally degradable flocculants. This is carried out at elevated temperature, which in turn causes thermal degradation, influencing the quality of the product. Starting from experimental results and the probabilistic nature of the process stochastic model was established to identify the rate and the mechanism of degradation under various conditions. It was concluded that applying moderate temperature around 143 °C ensures sufficient production rate without excessive thermal degradation.

INTRODUCTION

During chemical modification of starch to produce environmentally friendly flocculants, elevated temperature together with chemical agents are applied to achieve appropriate product. Heating generally causes thermal degradation, which is necessary to make the product soluble in water. However, beyond a certain extent of degradation, this may disadvantageously influence the quality of the product. In order to prepare high quality flocculants, we have to keep the highest possible molecular weight which is still soluble. To achieve this requirement, the conditions of treatment, namely temperature and processing time should be optimized. Besides experimental investigation, theoretical study by modeling the process helps to achieve this objective.

EXPERIMENTALS

In order to produce environmentally friendly anionic flocculants, degradable in the nature, corn waxy starch (Meritena 300, Hungrana, Hungary) was modified by partial substitution of the OH groups in the anhydroglucose monomer units with phosphate groups by laboratory experiments (Dencs et al. 2003). The chemical reaction was performed in the solid phase at elevated temperatures, where the phosphorylation and heat degradation of the starch took place simultaneously. Due to this process, the molecular weight distribution has decreased from the original 50-100,000 MDa to a range between 1-20 MDa.

At first, the native starch samples were impregnated with the aqueous solution of sodium diammonium phosphate and with N-containing catalysts in mortar. Then the samples

were dried and put into a block thermostat at various temperatures for different periods. The applied temperatures and processing times were changed between 135 and 150 °C, and from 5 to 270 minutes, respectively, as shown in Table 1.

Table 1: Experimental conditions

		Duration of the heat treatment, minutes																	
		5	10	15	20	25	30	40	50	60	75	90	105	120	150	180	210	240	270
Temperature, °C	135			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	138			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
	140			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
	143		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
	145	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
	148	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
	150	+	+	+	+	+	+	+	+	+	+	+	+	+					

The progress of the chemical reaction was followed by determining the chemically bound phosphorous content in the starch phosphate samples. After extracting the free phosphate, the analysis was carried out from the ash by Biochrom 4060 spectrophotometer. The electric charge density of the obtained starch phosphates, as well as their flocculation characteristics were studied in separate study, discussed by Dencs *et al.*, (2003).

The degradation was examined by measuring the molecular weight distributions in the resulted products. For this, starch phosphate samples of identical weights were dissolved in distilled water at 95 °C for 24 h (0.05 g starch in 5 mL water) and were analyzed by HPSEC/MALLS/RI. The relative quantities of the soluble part of the samples, i.e. the output of phosphorylation and degradation process were determined from the area below the RI chromatograms. The molecular weight distributions were obtained from the shapes of the chromatograms by Discovery 32 software. The mean molecular weights of the products were calculated both on weight and number averaging basis.

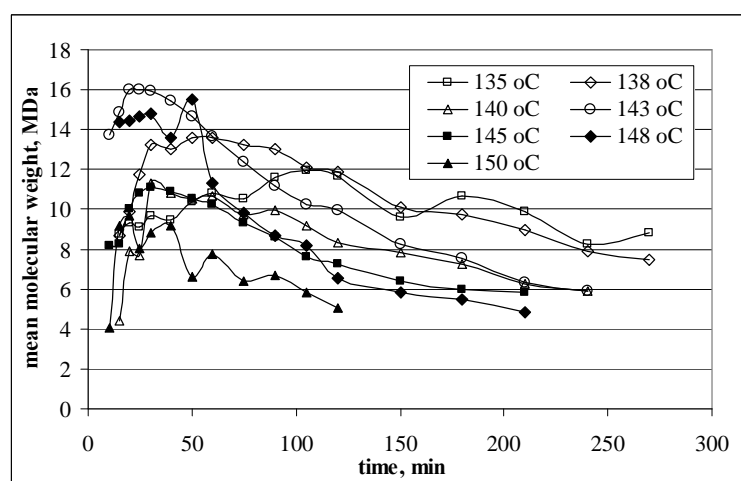


Fig.1: Change of the mean molecular weight during the treatments

From the results of the laboratory experiments it was concluded that, apart from a few controversial data in the initial period, the mean molecular weight was decreasing with increasing processing time and temperature as seen in Fig. 1. The output of the soluble compounds in the treated samples relative to the maximal achievable product quantity was increasing with rising temperature and by elongating the treatment. Fig. 2 shows the

relative areas below the RI chromatograms relative to the maximal achievable product quantity, in function of time and temperature.

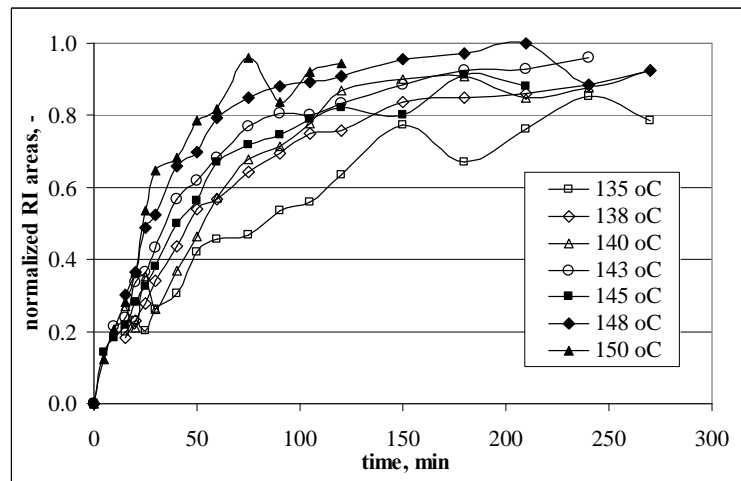


Fig.2: Dependence of the amount of soluble product on the process parameters

Depending on the conditions, the molecular weight distributions of the products were also changing. Fig. 3 shows some typical examples obtained at 143 °C after different treating times. To explain these variations, creation of an adequate mathematical model was inevitable. The basic principles for modeling were deduced from the results of the experimental studies.

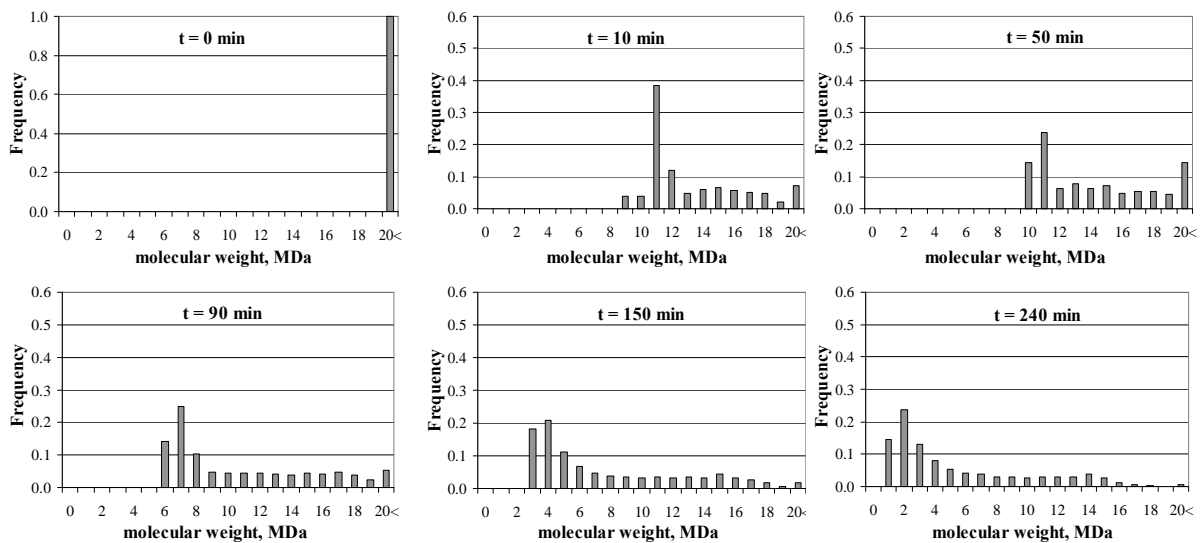


Fig.3: Examples for the changes of molecular weight distribution during the treatment

MODELING OF THE DEGRADATION PROCESS

From the results of the experiments it was recognized that, depending on the temperature and duration of the treatment, the rate of degradation and the shapes of the resultant molecular weight distributions were quite different. From respect of product quality not only the mean molecular weight, but its standard deviation are important features: the narrower is the distribution and the higher is its mean value, the better is the applicability for flocculation processes.

In principle, considering various degradation mechanisms, different distributions could evolve. From this respect, the location of splitting in the starch molecules has of primary importance. Starting from a narrow initial size distribution e.g., splitting at the middle of the molecules will lead to new size distribution, which will be also narrow. If splitting can take place at any part of the molecule with uniform probability, the resultant new distribution will be much broader. Deliberation of small groups from the molecules e.g. splitting at the ends of the chain will result in even broader and bimodal distribution.

Therefore, supposing a given mechanism, the resultant molecular weight distributions can be predicted by an adequate mathematical model. Or inversely, if the distributions are known from experiments, the ruling degradation mechanism can be determined by the model.

Preliminary Considerations and Neglections

In creating the mathematical model the following suppositions were made:

- ❑ The splitting of a given molecule among the multitude of other species is a stochastic event, i.e. it may happen accidentally. During a time interval, splitting has a given probability, depending on the chemical structure of the molecule, also influenced by the conditions in the reaction mixture.
- ❑ The location of splitting within the molecule may also be accidental, meaning that splitting off different parts from the carbohydrate chain can happen with certain probabilities, showing a probability distribution along the structure or length of the molecules.
- ❑ Due to the huge number of molecules present in the raw material or in the products, the molecular weight distribution can be considered quasi continuous one. However, to avoid the excessive complexity of the model, this can be simplified to a histogram by dividing the whole molecule weight range into discrete intervals.
- ❑ It was supposed that the transformation probabilities of a molecule belonging to a given molecular weight interval to smaller ones depend only on its actual state and do not change with time. In other words, the degradation process can be considered as homogeneous Markov chain.
- ❑ The variation of molecular weight or chemical structure within a discrete interval was neglected.
- ❑ It was also supposed that the transformation of the molecules goes on by splitting only. If, however, polymerization also happens, this can be considered by lowering the net degradation probability values, essentially not affecting the use of the model.

The Applied Model

Based on the considerations above, a new theoretical model was constructed for the studied degradation process, based on the stochastic approach suggested by Inoue and Yamaguchi (1970) and by Gyenis and Kátai (1990) for solids mixing problems.

The principle of the model is shown in Fig. 4, considering four discrete molecular weight intervals (M_1 - M_4) for the products and one for the raw material (M_0). The boxes in the Figure correspond to the mass fractions of material belonging to given intervals at a given moment and the arrows between them represent the transition of certain material fractions between the intervals. At the start, all the material to be treated (but not necessarily all) can be in interval M_0 . Within an arbitrary time step during the degradation process various fractions of this material can be transferred to other intervals of lower molecular weights (M_1 , M_2 , M_3 , M_4), according to their transition probabilities.

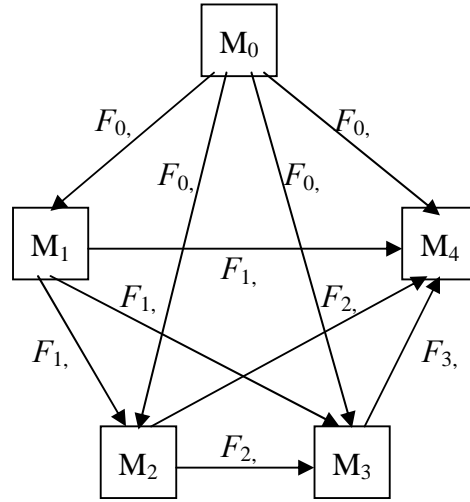


Fig.4: Transitions between the different molecular weight intervals

Since the process is considered as stochastic one, the temporary distribution of the material among the different molecular weight intervals after the n th time step (in time interval t_n) is also probabilistic, thus represented by a state probability vector $p(t_n)$, where $p_i(t_n)$ is the probability that unit quantity of material belongs to the i th molecular weight interval at that time.

$$p(t_n) = [p_0(t_n) \quad p_1(t_n) \quad p_2(t_n) \quad p_3(t_n) \quad p_4(t_n)] \quad (1)$$

This state probability vector corresponds to the expectable weight distribution of the material among the different intervals at a given time.

The chance that unit quantity of material belonging to the i th molecular weight interval will be transformed to the j th interval during a time step Δt is denoted by transition probability $P_{i,j}$. Diagonal elements $P_{i,i}$ denote the probability of remaining in the i th interval. All these probabilities are summarized in a transition probability matrix P .

$$P = \begin{pmatrix} P_{0,0} & 0 & 0 & 0 & 0 \\ P_{0,1} & P_{1,1} & 0 & 0 & 0 \\ P_{0,2} & P_{1,2} & P_{2,2} & 0 & 0 \\ P_{0,3} & P_{1,3} & P_{2,3} & P_{3,3} & 0 \\ P_{0,4} & P_{1,4} & P_{2,3} & P_{3,4} & P_{4,4} \end{pmatrix} \quad (2)$$

The expected weight distribution of the material or the state probability after the n th time step can be calculated by Eqn. (3), accordingly to other stochastic models used e.g. by Inoue and Yamaguchi (1970):

$$p(t_n) = p(t_0) \times P^n \quad (3)$$

where $p(t_0)$ is the initial state probability, or initial molecular weight distribution.

The expected value of the transformed mass fraction F_{ij} from the i th to the j th interval in the n th time interval is:

$$F_{ij} = p_i(t_n) \cdot P_{i,j} \quad (4)$$

Decreasing the time step Δt infinitesimally, the calculation can be carried out by solving a differential equation system where one of the composing equations referring to the change of state probability $p_i(t)$ is:

$$\frac{dp_i}{dt} = \sum_{j,j \neq i} (P_{j,i} \cdot p_j) - p_i \sum_{j,j \neq i} P_{i,j} \quad (5)$$

RESULTS AND DISCUSSION

To define the molecular weight intervals by dividing the whole size range into several ones, any kind of division e.g. linear, exponential, or even not regular scale can be used. Considering the measured distribution data where very small molecule fragments were generally absent for a considerable long period after starting the process, it was supposed that fragmentation takes place by splitting the molecules around their middle region. Therefore, in the study reported here exponential scale was used by halving the interval limits repeatedly. Four intervals were defined for the degradation products, ranging between 16-32 (M_1), 8-16 (M_2), 4-8 (M_3), and 2-4 (M_4) million Dalton (MDa), respectively. Fragments below 2 MDa were measured in a few cases only, in negligible quantities. Therefore, no interval below 2 MDa was considered in the model. Measured data between 32-16 MDa had some uncertainty, because of the limited water solubility of the material above 20 MDa during sample preparation for the analysis.

Since the original starch was insoluble in water, the same difficulty arose regarding its analysis by the applied HPSEC/MALLS/RI method without chemical modification. The lack of knowledge on its exact molecular weight distribution constrained us to consider the first M_0 compartment as a black box with 32 MDa lower and indefinite upper limits. To normalize the distribution data in the M_0 - M_4 intervals, the maximal achievable amount of the water soluble product was used as normalizing factor, keeping the material balance.

In order to investigate the degradation process, computer simulations were carried out by ModelMaker software (Cherwell Scientific) using the model described above. The values of the transition and state probabilities were found out by fitting the experimental and simulated data using trial-and-error method. As a result, quite good agreement was achieved between the measured and simulated data (0.05 – 0.07 w/w or 5.2 – 7.5 per cent relative standard deviation) for the studied conditions. Fig. 5 shows a typical example for the variation of the measured and simulated weight fractions in function of time for various molecular size intervals, obtained for heat treatment at 145 °C.

Table 2 shows the transition probabilities obtained for the best fits of the experimental and simulated data. The transition probabilities shown in Fig. 4, but not listed in Table 2 proved to be zero. From the values shown in Table 2 the degradation probabilities P_i of the material in any i th molecular weight interval were determined from the $P_{i,j}$ values by Eqn. 6.

$$P_i = \sum_j P_{i,j} \quad (6)$$

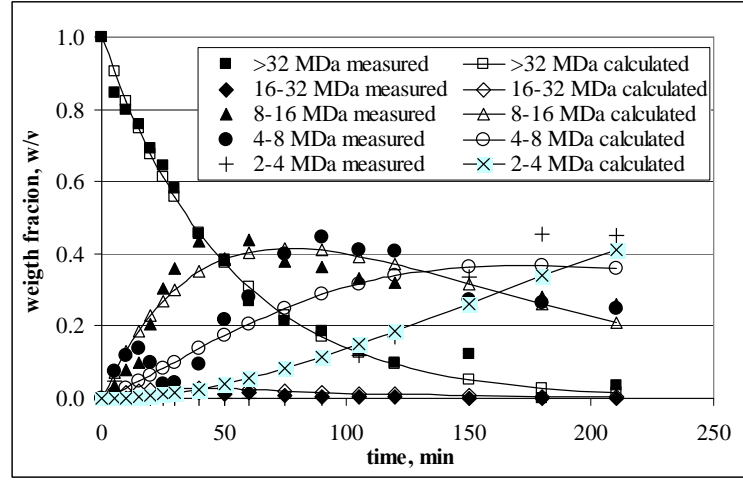


Fig.5: Measured and simulated data for heat treatment at 145 °C

Table 2: Transition probabilities between different molecular weight intervals

Transition probabilities, w/w/min	Temperature of the heat treatment							
	135 °C	138 °C	140 °C	143 °C	145 °C	148 °C	150 °C	
$P_{0,1}$	0.0020	0.0050	0.0010	0.0090	0.0020	0.0080	0.0010	
$P_{0,2}$	0.0100	0.0100	0.0150	0.0120	0.0150	0.0130	0.0150	
$P_{0,3}$	0.0000	0.0000	0.0010	0.0000	0.0025	0.0020	0.0150	
$P_{1,2}$	0.0003	0.0003	0.0013	0.0013	0.0100	0.0050	0.0100	
$P_{1,3}$	0.0030	0.0070	0.0130	0.0130	0.0250	0.0120	0.0250	
$P_{2,3}$	0.0060	0.0035	0.0075	0.0035	0.0075	0.0060	0.0060	
$P_{2,4}$	0.0000	0.0002	0.0012	0.0015	0.0012	0.0005	0.0005	
$P_{3,4}$	0.0015	0.0020	0.0032	0.0045	0.0060	0.0065	0.0120	

Degradation probabilities calculated by Eqn. 6 showed significant rise with increasing temperature, and were decreasing with diminishing molecular weights as shown in Fig. 6.

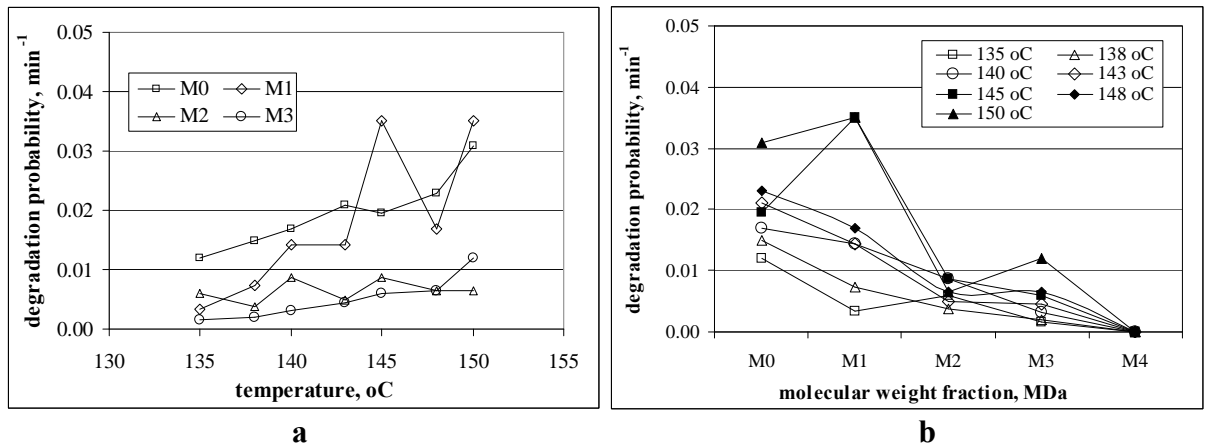


Fig.6: Degradation probabilities depending on the temperature and molecular weight

Considering the transformation probabilities from given molecular weight intervals to other intervals, the ruling mechanism of the process can also be identified. Molecules with lower sizes (intervals M_2 and M_3) split most probably into two pieces, around their middle, because the daughter molecules will mainly be transferred into the next intervals (M_3 and M_4), respectively. However, from the intervals of higher molecular weights (M_0 and M_1) the most probable transformation takes place towards the second next intervals (to M_2 and M_3 , respectively), suggesting that these molecules break most likely into 3 or more pieces, thus not always at their middle region. From the intervals of high molecular weight direct formation of small fragments has no probability at all.

CONCLUSIONS

From the results of simulation it was concluded that the degradation probabilities in the studied 135-150 °C temperature range were increasing with increasing temperature and were reduced significantly with decreasing molecular weight.

From the probabilities of transitions from given molecular weight intervals to others, conclusions were drawn to the probable mechanism of the degradation.

Studying the molecular weight distribution of the products obtained at different temperatures and treating times, it was concluded that moderate heat treatment around 143 °C results in sufficiently high production of water soluble starch derivate (about 80 % of the maximal achievable yield) within reasonable time (75 min). The product obtained here had 12 MDa mean molecular weight and relatively narrow size distribution between 7 and 20 MDa (with STD 4.3), suitable for environmentally benign flocculants.

NOMENCLATURE

M_i	i th molecular weight interval
F_{ij}	weight fraction transformed from interval i to interval j in unit time, w/w/min
$p(t_n)$	state probability vector defined by Eqn.1.
$p_i(t_n)$	probability that unit quantity of material belongs to the i th interval, dimensionless
P_{ij}	transition probability from an i th to a j th interval during a Δt time step, w/w/min
P	transition probability matrix defined by Eqn.2.
t_n	time after the n th time step, min
Δt	time step, min

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