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A STUDY ON THE RATE AND MECHANISM OF THERMAL DEGRADATION OF STARCH IN PRODUCTION OF FLOCCULANTS

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Experiments and theoretical study were carried out to investigate the degradation rate and mechanism of starch molecules to establish suitable conditions of producing biodegradable flocculants by phosphorylation at elevated temperatures. The whole molecular weight range of original starch and the possible starch derivatives was divided into five intervals using an exponential scale. A Markov-chain stochastic model with transition probabilities from the higher molecular weight categories to the lower ones was proposed to analyze and explain the experimental findings. By fitting the model to the experimental data the transition probability values were determined for the studied process conditions. From these conclusions were drawn for the kinetics and possible degradation mechanism. It was concluded that the degradation of the molecules took place by splitting the molecules to several pieces, but no end-chain-scission mechanism was present under the studied conditions.

Keywords: Starch, thermal degradation, stochastic model, flocculants.

Introduction

During chemical modification of starch to produce environmentally friendly flocculants, elevated temperature with chemical agents are applied to achieve appropriate product. Heat and chemical agents together cause essential modification and degradation of the chemical structure of the original molecules. Besides the formation of anionic groups on the resultant molecule fragments, a suitable decrease in their molecular weight is necessary to make the product soluble in water. However, excessive degradation may influence disadvantageously the quality of the product. In order to prepare high quality flocculants, we have to obtain a relatively high molecular weight with narrow distribution which is still soluble. In order to fulfill these requirements, the conditions of treatment, especially the pH, the temperature and the processing time should be optimized. In addition to experimental investigation theoretical study and modeling of the process can help to achieve this objective.

The mechanism of degradation highly influences the molecular weight distribution during the treatment. Therefore, research works to elucidate the possible ways or mechanisms of molecule splitting have come into the limelight in a lot of recent studies dealing with the degradation of various polymeric materials in different treatments. Studying the thermal degradation of linear polymers, Staggs [1] has developed a mathematical model for the random scission at different positions of the polymeric chains in the form of a set of ordinary differential equations. This model proved to be suitable to describe the evolution of molecular weight distribution as a function of the fraction of bonds broken. In another work of this author a mathematical model has been constructed to analyze the evolution of the population of molecules in case of simultaneous end-chain scission and their recombination [2]. Model predictions on the evolution of the molecular weight distribution well agreed with numerical Monte-Carlo simulations and experiments. As regards Monte-Carlo simulations, a molecule was selected at random from a distribution of molecules and allowed to undergo end-chain scission, generating a monomer and a new molecule with one fewer repeat units. Madras et al. [3] investigated the rate of degradation of PMMA polymer, dissolved in toluene, at different temperatures in tubular flow reactor. A discrete model for the first-order rate of polymer degradation was derived and compared to the continuous kinetics approach. In another work Madras et al. [4] studied the effect of the molecular weight on the dynamics of polystyrene degradation. It was supposed that the dynamics of polymer decomposition by random-chain scission depend on the molecular weight of the degrading polymer molecules. Measurements were carried out with monodisperse polystyrene changing the initial molecular weight from 12 MDa to 930 MDa. Based on the results relating to the time evolution of the molecular weight distribution equations were proposed to determine the rate of degradation. As a result of this investigation the rate coefficients proved to be a second-degree polynomial function of the initial molecular weight. Besides the widely studied random scission type degradation of polymers Kostoglou [5] emphasized the importance of the chain-end scission mechanism. Considering that the breakage population balance equation provides effective and simple means to analyze the change of the molecular weight distribution during the degradation processes various models (continuous, discrete-continuous and corrected continuous models) were developed to analyze the evolution of the product molecular weight distribution.

Ziff and McGrady [6] have found that the rate of bond scission depended on the total chain length as well as on the position of the bond within the chain. A model was proposed and solved where the chain bonds break preferentially in the center with a parabolic probability distribution.

A Monte Carlo study of the degradation of highly branched polymer molecules was published by Galina and Lechowicz [7]. The aim was to verify whether a bond scission led to a split of molecule into two smaller ones or just to reduction in the number of monomer units in the original molecule. The splitting probability of a bond was supposed to be increasing with the substitution degree of the given unit in the molecule. It was pointed out that under the given conditions each degradation step for acyclic molecules led to a split of molecules into smaller components and the average size of molecules decreased rapidly from the very beginning of the process. An interesting work was reported by Emsley and Heywood [8] too, on computer modeling of the degradation of linear polymers. They used pseudo-random number generator to carry out Monte Carlo simulation of the process. Randomly chosen bonds were split either at random positions along a molecule or breaking the molecule in half or slicing off a fixed number or percentage of units. The resulting molecular weight distributions were compared to experimental measurements relating to the degradation of cellulose in water. It was found that totally random processes did not explain the experimental findings, especially related to the new peaks in the resulted molecular weight distribution and their movements in function of time toward lower molecular weights. A supposed mechanism simulated by systematic scission of polymer chain has led to much better agreement. Peak movement was explained by preferential scission of the longest molecules.

As regards modeling, the most of the studies in polymer science done till now preferably applied deterministic models based on exact chemical reaction equations or on momentum equations used for the molecular weight distribution. Only a few works were there proposing random models with Monte-Carlo simulation. Nassar et al. [9] applied Markov-chain approach for stochastic analysis of stepwise enzymatic cellulose degradation. The model has predicted the change of the number or concentration distribution of cellulose chains according to their lengths obtained by hydrolysis after different times. However, several Markov-chain models have been developed in other fields of chemical engineering such as to investigate the mixing of particles [10] or particle attrition or breakage [11, 12]. From respect of modeling principles particle breakage is very similar to the degradation of molecules. During this processes it can be supposed that the splitting of a molecule, similarly to the breakage of particles, can not be considered as deterministic one. Therefore, stochastic models have a great potential in the analysis and understanding of the degradation of large molecules of natural origin, such as in a complex mixture of starch molecules, because their exact structures and molecular weight distribution is not known in depth.

Experiments

In order to produce environmentally friendly i.e. biodegradable anionic flocculants, corn waxy starch was modified by partial substitution of the OH groups in the anhydroglucose monomer units with phosphate groups in laboratory experiments [13, 14]. The chemical modification was carried out in the solid phase at elevated temperatures, where the phosphorylation and heat degradation of the starch took place simultaneously. During this process, the original molecular weight range of 50-100 MDa of the native starch samples has decreased to a range of 2-20 MDa.

As regards the raw material of these experiments Meritena 300 corn waxy starch supplied by HUNGRANA Ltd. (Hungary) was used. All reactants used for the experiments were of analytical grade bought from Merck AG.

To carry out the modification the original starch samples were impregnated with the aqueous solution of diammonium hydrogen phosphate and N-containing catalysts in a 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 ^{o}C, and from 5 to 270 minutes, respectively. The progress of the phosphorylation reaction was monitored by determining the chemically bound phosphorous content in the samples taken from the reaction products. After extracting the free phosphate, the analysis was carried out by Biochrom 4060 spectrophotometer from the ash obtained by heating the samples in a furnace.

The change of the molecular weight distribution was monitored by size exclusion chromatography. The molecular weight distributions of the resulted starch phosphate products were determined as follows: samples of identical weights were dissolved in distilled water at 95 ^{o}C for 24 h (0.05 g starch in 5 mL water) and were analyzed by HPSEC/MALLS/RI as was described in detail by Meiczinger et al. [14]. The relative quantities of the soluble part of the samples, i.e. the outputs of phosphorylation /degradation process were determined from the area below the RI chromatograms. The molecular weight distributions were calculated from the chromatograms by Discovery 32 software. The mean molecular weights of the products used in this paper were calculated on weight averaging.

Mathematical model

Because the breakage of individual molecules and the position of splitting within the molecule has to be supposed accidental, and the degradation process as a whole is influenced by local variables within the reaction mixture that are also random in certain extent, a Markov-chain stochastic model was proposed for this study described in more detail in another paper by Gyenis et al. [15]. The principle of the applied method is shown in *Figure 1,* where the nodes of the graph (the square boxes) denote discrete molecular weight intervals or categories changing from M_5 to M_1, where M_5 is the highest and M_1 is the lowest molecular weight range. In these boxes different weight fractions of the whole reaction mixture are present at a given moment of the process. The edges of the graph (the arrows between the boxes) represent the weight fraction transitions between the boxes, i.e. from given molecular weight categories to the other ones that can happen with certain probabilities. As is seen from the direction of the arrows, only degradation is considered here, i.e. transitions from higher molecular weight intervals to the lower ones can take place only. If, simultaneously with the degradation, polymerization or coupling of certain molecules would also take place, this does not affect this model essentially, because the arrows represent net transitions, and in this case the rate of degradation is always higher then that of the polymerization.

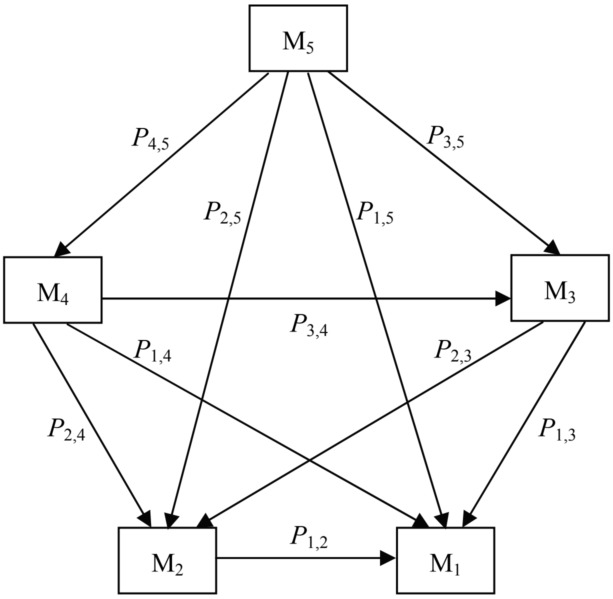

Fig.1. Principle of the applied mathematical model.

As was explained in another paper [15], the division of whole molecular weight range to smaller intervals can be done arbitrarily, i.e. the spans of these intervals should not be necessarily identical. Because, during the experiments the molecular weight axis of the measured chromatograms had an exponential scale whose linearization could cause some uncertainty in the molecular weight distribution data, we used exponential scale in the model, too, with the following molecular weight intervals decreasing from M_5 to M_1:

$$M_5 > 32\ \text{MDa} > M_4 > 16\ \text{MDa} > M_3 > 8\ \text{MDa} > M_2 > 4\ \text{MDa} > M_1 > 2\ \text{MDa} \tag{1}$$

This scale was obtained by stepwise halving of the lower limits of the previous molecular weight intervals.

The transition probabilities between the various molecular weight intervals during a given time interval are summarized in a matrix shown in Eqn.1, where a matrix element $P_{j,i}$ refers probability of material transition from interval i to interval j.

$$P = \begin{vmatrix} P_{5,5} & 0 & 0 & 0 & 0 \\ P_{4,5} & P_{4,4} & 0 & 0 & 0 \\ P_{3,5} & P_{3,4} & P_{3,3} & 0 & 0 \\ P_{2,5} & P_{2,4} & P_{2,3} & P_{2,2} & 0 \\ P_{1,5} & P_{1,4} & P_{1,3} & P_{2,1} & 1 \end{vmatrix} \tag{2}$$

The quantities of material being in the molecular weight intervals or categories are accounted in mass or weight fraction units. If all the material is present only in one of these intervals (say in the i^{th} interval), it means that the weight fraction being in this interval is 1 (unity), and the weight fractions in all other intervals are zero, because their sum in all intervals should be unity. In case of an arbitrary distribution between the intervals, the expected weight fraction transition during a Δt time step from interval i to interval j is

$$\Delta x_{j,i} = P_{j,i} \cdot x_i \cdot \Delta t \tag{3}$$

Supposing an initial molecular weight distribution between five molecular weight intervals in the initial state at time t_0 (t=0):

$$p(t_0) = \left[p_5(t_0) \quad p_4(t_0) \quad p_3(t_0) \quad p_2(t_0) \quad p_1(t_0) \right] \tag{4}$$

the probable molecular weight distribution after the *nth* time step (t=t_n) is

$$p(t_n) = \left[p_5(t_n) \quad p_4(t_n) \quad p_3(t_n) \quad p_2(t_n) \quad p_1(t_n) \right] \tag{5}$$

that can be estimated by the equation proposed by Inoue and Yamaguchi [16] in a stochastic model of solids mixing:

$$p(t_n) = p(t_0) \times P^n \tag{6}$$

The probability of the degradation of the molecules being in the i^{th} molecular weigh category is the sum of the transitions probabilities from that category to all other molecular weight intervals:

$$P_i = \sum_j P_{j,i} \tag{7}$$

The details of application of this model are discussed in [15].

Results and discussion

As a result of laboratory scale experiments *Figure 2* shows the variation of the relative yields of the water-soluble degradation products as a function of time at various reaction temperatures compared to their maximal achievable amount measured during this investigation, which was almost 100 per cent of the treated starch sample. The total amounts of these soluble fractions were determined from the RI areas of the chromatograms. From Figure 2 it can be seen that the total yields have increased with the duration of the treatment, and were also increasing with rising the reaction temperature from 135 °C to 150 °C.

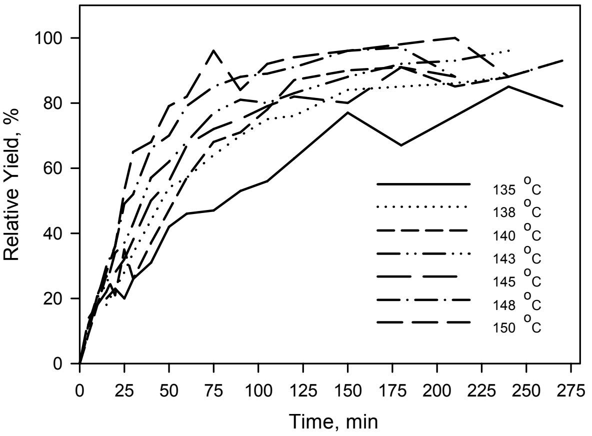

Fig.2. Variation of the water soluble product yield in function of time at various temperatures

Beside the well recognizable tendencies certain irregularities can also be observed in this diagram, due to unexplored effects that could come from the stochastic nature of degradation of the molecules, but most likely from the possible irregular variation of the local conditions during the process that may be distributed not homogeneously within the reactor.

Figure 3 shows the changes of the mean molecular weights of the samples during the process, calculated from the measured molecular weight distributions in function of the reaction time at various treatment temperatures. From this, it is seen that the mean molecular weight decreases continuously with increasing time. The temperature of the treatment had also crucial influence, because elevated temperatures caused considerable stronger degradation which resulted in lower molecular weights in the product. Certain accidental variations in these curves also refer to unidentified influences during this treatment mentioned above.

Another difficulty during the measurements came from the very low solubility of samples at the very beginning of the process, which can cause reduced reliability of the results gained by the analysis after short reaction times. The samples at the very beginning e.g. below 25 min contained only a negligible quantity of soluble components with relatively high ratios of small molecule debris of not identified origin. Therefore these data was disregarded and not shown in this diagram.

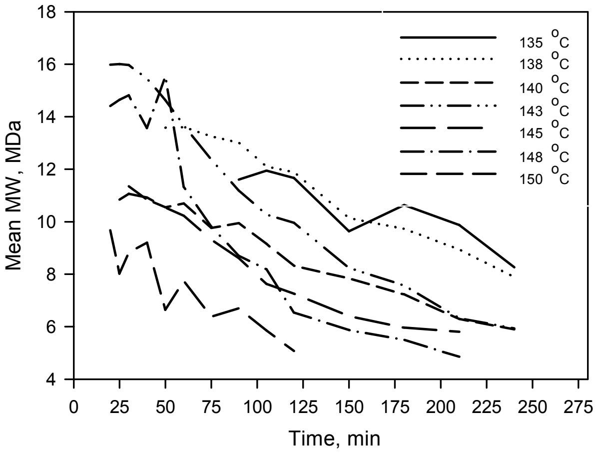

Fig.3. Change of the mean molecular weight of the obtained water soluble starch derivatives

From the samples obtained after longer treatment times the time evolution of the weight ratios in the five fractions M_5-M_1 was determined for all reaction temperatures. For this, the weight fractions in M_4-M_1 were obtained from the chromatograms, while the weight fraction of the insoluble starch above 32 MDa i.e. in M_5 category was determined from the material balance. It should be noticed that the amount of molecule fraction below 2 MDa was negligible small for all the temperatures and reaction times studied, therefore a possible sixth category between 0 and 2 MDa was disregarded.

For all reaction temperatures, the weight fraction above 32 MDa, i.e. in the highest molecular weight category rapidly decreased in function of time that is shown in *Figure 4* as an example for the experiments carried out at 145 °C. Reaction product between 2 and 4 MDa i.e. in category M_1 was observable after a relatively long time at almost all reaction temperatures. At 145 °C e.g. this time delay was more than 100 min. The only exception was observed at 150 °C, the highest reaction temperature studied where this molecular weight fraction appeared just at the very beginning of the process.

The amounts of the intermediate fractions M_4-M_2 showed a relatively rapid rise in the first period of treatment at almost all the studied reaction temperatures, then going through a maximum. At higher temperatures, at 143 °C and above, fraction M_4 between 32 and 16 MDa practically did not appeared because it was bypassed or too rapidly transformed to lower molecular weight fractions. As it will be shown later, modeling gave a help to elucidate the reason of this observation. Although Figure 4 referring to 145 °C reaction temperature gives a representative example of these experimental data, more experimental results were shown and discussed in details in an earlier publication [17].

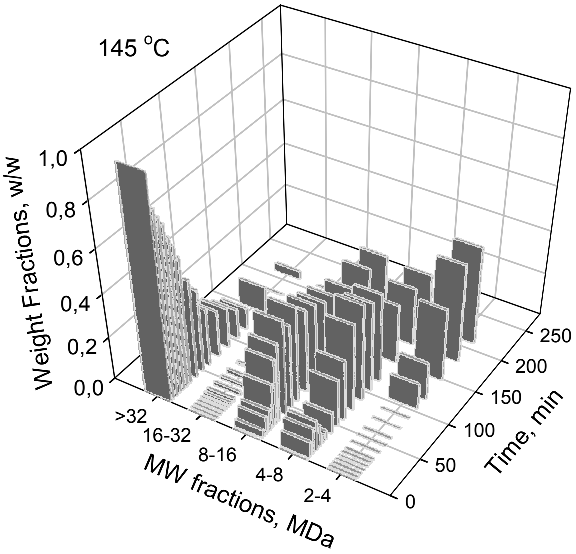

Fig.4. Evolution of weight fractions of the treated material in different molecular weight categories at 145 °C.

To elucidate the mechanism dominating during the studied degradation process simulations were carried out by using the stochastic model shown above. By changing the values of transition probabilities $P_{j,i}$ it was possible to study their effect onto the time evolution of the relative quantities of the studied molecular weight fractions in the reaction products. In this study various suppositions were made regarding the distribution of the splitting probabilities along chains of the starch molecules for different molecular weight fractions [15].

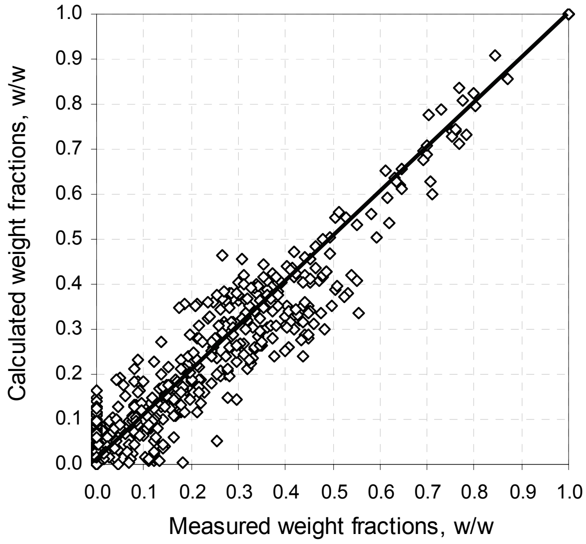

Fig.5. Comparison of the measured and calculated weight fractions obtained by fitting the model

Using a trial and error fitting method, a series of parameter identification were carried out by minimizing the standard deviation between the measured and calculated data. By this, the transition probability values that gave the best fit were determined for each experimental condition [17]. *Figure 5* gives a comparison between the measured and calculated weigh fractions of the five molecular weight categories (M_5-M_1) for all reaction times and temperatures studied here. The mean deviation between the measured and calculated weight fractions was 0.047 w/w. This seems to be reasonable for such a complex reaction system, considering the stochastic nature of the studied system, and the difficulties of the analysis at the beginning of the process.

Analyzing the obtained transition probabilities deductions were made regarding the possible mechanism of the degradation process. *Figure 6* gives an example for the $P_{j,i}$ values for the reaction temperature of 145 °C. A column in this diagram gives the probability of mass fraction transition from given initial molecular weight range to another one during unit time.

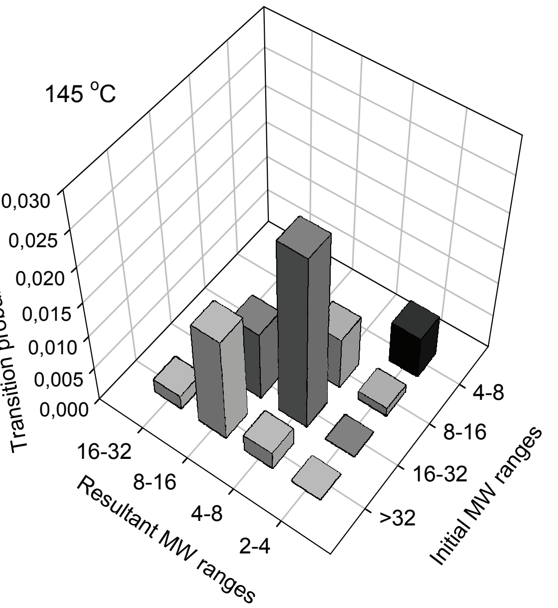

Fig.6. Example for the transition probabilities between different molecular weight categories determined by model fitting for 145 °C reaction temperature

From this Figure the following information can be read out: The transition of the material from the highest original molecular weight range above 32 MDa is most probable to the category with molecular weight limits of 8-16 MDa. Because during the simulation made by a differential equation solver (ModelMaker®) very small time steps were used, it can rightly be supposed that the initial molecules split into at least 2-3 fragments of similar lengths in one reaction. Transitions to molecular weight ranges of 16-32 and 4-8 MDa occur with much less probabilities. This latter transition means that splitting into 4 or more pieces (e.g. from 32 to 8 MDa) is also possible. The occurrence of transitions from the >32 MDa category into the 2-4 MDa is negligible small, therefore splitting off small molecule fragments from the original molecule chains e.g. by end-scission mechanism is not very probable. From these probability data it seems that splitting take place mainly along the inner regions of the molecules, meaning that end-scission mechanism is not dominant under the studied reaction conditions.

From these data it can also be supposed that there should be certain degradation inside the highest molecular weight category (above 32 MDa) whose products still remain within this category (when e.g. a molecule of 100 MDa splits into two fragments with 60 and 40 MDa molecular weights). Unfortunately, the available analytical methods have not allowed us to explore the molecular weight distribution and its changes inside this >32 MDa range. But, during self-transitions within this category similar mechanism can be supposed, i.e. by splitting about the inner regions of the molecules without significant end-chain-scission, because practically no direct transitions were found from the >32 MDa category into the lowest molecular weight ranges of 2-4 MDa or below.

As regards the fragmentation of the molecules being in molecular weight range 16-32 MDa, similar mechanism can be supposed, because transition into the category of 4-8 MDa looks dominant (by splitting the molecules to minimum 2 and maximum 8 fragments) together with certain transition into the range of 8-16 MDa (by splitting to minimum 2 and maximum 4 pieces). The probability of transition to the smallest 2-4 MDa category is negligible here. End-scission mechanism is therefore not likely in this 16-32 MDa molecular weight fraction.

The situation is similar for the 8-16 MDa category because, most probably, the molecules split here to 2-4 pieces, i.e. the majority of fragments are transferred to the range of 4-8 MDa. The transition probability values in this category are much lower than those in higher molecular weight categories. It is also true for the molecules in category of 4-8 MDa that are tending to split with relatively low probability to 2 pieces only. Due to this decaying transformation rate tendency, the product molecules accumulate within the two or three smallest molecule weight ranges below 16 MDa towards the end of the process, as is seen in Figure 4 after 150 min treatment. For that time the resultant product belongs to a rather narrow molecular weight range with almost uniform occurrence between 16 and 2 MDa. Smaller fragments are not present, which is favorable to use this product as high quality flocculants. Stopping the process earlier, e.g. somewhere between 50 and 100 min the molecular weight distribution of the product will have even narrow, between 16 and 4 MDa under the studied conditions.

The proposed mechanism was similar for the other reaction temperatures, too. As regards the kinetics of the process, *Figure 7* shows the dependence of the degradation probabilities, determined according to Eqn. 6, in function of reaction temperature and molecular weights. From this data it is clear that the largest molecules belonging to the >32 MDa category degrade most probably thus resulting a very high transformation rate to smaller fragments. This primacy was observed especially at lower temperatures. The data referring to the category of 16-32 MDa show some extra high values especially at the high temperatures, but the breakage probability were not so high at lower temperatures. In case of lower initial molecular weights, namely in the range of 8-16 and 4-8 MDa the molecules showed more stability, their transformation toward lower MW categories are much lower. This situation does not change much with the increase of the temperature. Molecules in the range of 2-4 MDa proved to be very stabile and have no degradation tendency at all.

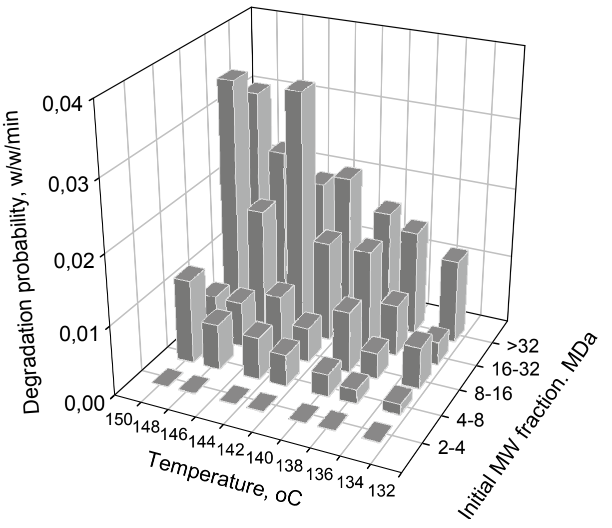

Fig. 7. Degradation probabilities of different molecular weight fractions at various treatment temperatures

As a whole, it is concluded that the probability of degradation decreases significantly with decreasing molecular weight and treatment temperature.

These results helped us to optimize the process conditions to produce flocculants from starch with appropriate molecular weight distribution. Temperatures 143-145 °C provided quite high degradation rate resulting in high product quality suitable for flocculants within reasonable treating time. At higher temperatures such as at 148 °C or above, lower molecular weight starch derivatives can be produced which can be utilized for natural-based anti-scale agents.

Conclusions

Experiments and simulations were carried out to investigate the rate and mechanism of the degradation of starch molecules in order to find out suitable conditions to produce biodegradable flocculants by simultaneous heat treatment and phosphorylation. For this study a Markov-chain stochastic model was proposed to explain the experimental data. The whole molecular weight range between the original >32 MDa and the lowest 2 MDa was divided into five intervals decreasing their widths or limiting MW values exponentially. By fitting the model to the experimental data the transition probability values were determined for the studied process conditions. From these latter, conclusions were drawn for the kinetics and possible degradation mechanism.

The degradation probability of the molecules being in a given molecular weight interval were increasing with rising treatment temperature and reduced significantly with decreasing molecular weight. As regards the possible mechanism, it was concluded that the transformation of the original starch molecules and its intermediate products took place by splitting the molecules to several pieces, and no end-chain-scission mechanism was detected under the studied conditions.

As a result of this study it was possible to optimize the conditions to obtain high quality flocculants with relatively narrow molecular weight distribution with mean values around10 MDa.

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SYMBOLS

M_i = molecular weight interval or category, characterized by their lower and upper molecular weight limits in MDa, -

P = mass transition probability matrix defined by Eqn.1

$P_{j,i}$ = mass fraction transition probability from molecular weight interval i to interval j, on weight basis, w/w/min

P_i = degradation probability of the molecules being in the *ith* molecular weight interval, on weight basis, w/w/min

$p(t_n)$ = state probability vector describing the expectable distribution of the material between different molecular intervals at time t_n,, w/w

$p_i(t_n)$ = probability that the unit weight fraction of the material is in the ith molecular weight interval at time t_n , w/w

x_i = expected weight fraction being in the *ith* molecular weight interval at a time, w/w

$\Delta x_{i,j}$ = expected weight fraction transition from the *ith* to the *jth* molecular weight interval during a Δt time step, w/w

Δt = time step, min

INDICES

i = index of the initial molecular weight category of a molecule before the degradation

j = index of the target molecular weight category of the fragment formed by degradation

n = the number of time steps from the beginning of the degradation process where the whole reaction time span is divided into N discrete time interval

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