Approach to mathematical model of the cross-linking reaction of polymer composite

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Abstract
The nature of the reaction of collagen with cross-linking agents is very important not only in leather technology, but also in nutritional industry. The question how to mathematically describe the reaction is still unanswered because at the present there neither is controlling the process, nor reliable measuring of its course. Paper should describe current state in this field and proposes a motion of the mathematical description of cross-linking reaction. Some simulations will be used for illustration of time dependencies of individual reactant concentrations.

Keywords: Condensing reaction, collagen hydrolyzate, glutaraldehyde, mathematical model, simulation

Introduction

At the present time, there are still industrial branches which can be called typical polluters in spite of the effort to reduce their negative impact on environment. Tanning industry is one of them and as a whole, it can not be covered with any list of steps that should contribute to environment protection. Tanning industry has various manufacturing sectors with specific impacts on surrounding. It is necessary to assert an individual approach during judgment of these impacts and to minimize negative influences in accord with the national legislation. Leather manufacturing produces considerable amount of wastes which means unfavourable impacts on elementary components of environment, especially soil, water and air. There are two ways how to solve this problem. The former is preventive way and leads to limitation of waste production by force of clear technology installation or recycling methods. Recycling procedure allows utilizing wastes as a source of secondary raw material without any reference to place or time of waste formation. The latter way removes consequences of industrial production which disturbs balance of nature or has negative impacts on environment. It is closely analysed in (Blažej at al. 1984). New conception of manufacturing from utilizing products and waste formation point of view brings many steps which prospectively results in installation of wasteless technologies. It means that the amount of wastes can be decreased by force of a suitable change of the original manufacturing process. It is spoken about high degree of material use and significant decrease of processing waste. These technologies can be considered as a specific case of recycling when neither time shift nor spatial shift arises between waste formation and their utilization. Amount of energy which is consumed for reutilization of waste should be minimal and demonstrates how the wasteless technology is effective. Wasteless technologies are based on conceptual solution of whole cycle: raw material – manufacturing – consumption – recycling of waste. Principle of solution is product with desiderative parameters which is produced with minimal material and energy usage. From practical point of view, the realization of wasteless technology is inaccessible. In practice, every technology of this type produces wastes in minimal amount, but they always have specific impact on environment. In general, material which can not be further used, is considered as waste. There is no problem to meet the term “environmentally waste-less technology”, which has not at least negative consequences for nature. Let us concentrate to leather manufacturing which ranks a specific position. It processes leather of fatstock and game, which are wastes of meat-processing industry. From this point of view, the leather industry is the first branch whose main raw material is waste from other industrial productions. However, in addition to valued product it produces considerable amount of liquid and solid wastes. By way of physical and chemical processes the leather is gradually transmuted into the hide. Production of 250 kg of hide requires 1000 kg of leather, more details can be found in (Kupec at al. 2000), (Covington 2001). Recovery factor stands 25%, which is quite low value. The rest comprises secondary products from which the hide trimmings and chrome-tanning shavings are the most valued (Langmaier 1974). These are very important raw material for another processing. For example, hydrolyzate of collagen is industrially produced from chrome-tanning shavings (originally minor waste product) by enzymatic hydrolysis. Utilization of collagen hydrolyzate can lie in the production of proteinaceous casings for nutritional industry; in particular, it is biodegradable casings used in butcher production. Production of clearly natural composite or copolymer is also considered. In this biodegradable material, collagen and vegetal fibres can comprise matrix. For example, these composites could replace plastic wraps and also could be used in wood industry as an adhesive material. In all mentioned applications, collagen hydrolyzate is supposed to be cross-linked with any suitable agent. This is absolutely the most important step during its processing. In this study, non-toxic and environmentally friendly glutaraldehyde was used (Lundblad at all. 1983). In practice, this process is realised discontinuously. Therefore for the mathematical modeling purposes we consider a batch reactor. Chemical reactors are very often used in industry, especially in chemical and biochemical divisions. Nowadays, computer simulations are often used because they have many advantages in contrast to an experiment on a real system, which is uneconomic and sometimes not feasible and can be dangerous. Some modeling methods are described by (Kolomazník 1990), other simplification, modeling

and simulation can be found in (Ingham at al. 1994). The simple differential method is presented by many authors, e.g. (Lyuben 1989), Runge-Kutta's integration method can be found in (Ralston 1979).

Scheme of the reaction

Reaction of collagen hydrolyzate with glutaraldehyde can be schematically described as follows:

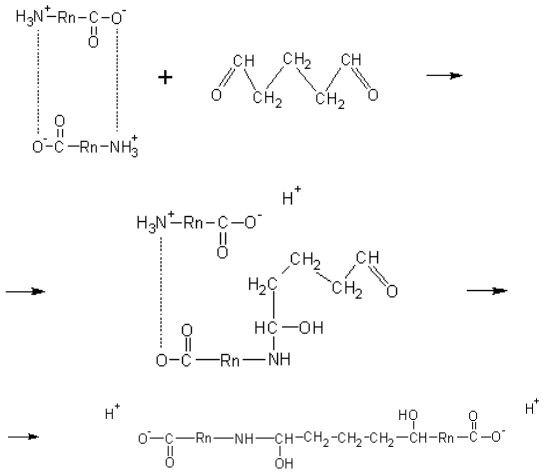
$$A + B \xrightarrow{k_1} C \xrightarrow{k_2} D \quad (1)$$

$$2A \xrightarrow{k_3} E \quad (2)$$

Cross-linking agent A reacts to protein B and as a result, intermediate product C arises. Intermediate then reacts to itself due to its two reactive bonds and final product D (prime material for production of biodegradable casings) arises. Simultaneously, glutaraldehyde reacts to itself (Aldol synthesis) and as a result of this reaction, aldol resins E arises. These resins have typical coloration so that this reaction is accompanied with colour change. Final product is supposed to be clear and colourless so that this aldol synthesis is undesirable. Coefficients k1, k2 and k3 are reaction velocities which are dependent on temperature according to Arrhenius law (3).

$$k_j = k_{oj} \cdot \exp\left(-\frac{E_j}{R \cdot T_r}\right) \text{ for j = 1, 2, 3} \quad (3)$$

where k0 [-] represents pre-exponential factors, E [J.mol^{-1}] means activation energies, R [J.K^{-1}.mol^{-1}] is universal gas constant and T [K] is absolute temperature. Due to some simplifications, all reaction velocities are considered as constant – reaction is considered at the same temperature.From the chemical point of view, collagen hydrolyzate is a product of skin collagen and contains seventeen aminoacids. The most important and mostly represented of them are glycine, proline and hydroxyproline. From this reason, for mathematical simulation the collagen hydrolyzate is considered as a copolymer of mentioned aminoacids, (Heidemann 1993). Condensing reaction can be described in a simplified way:



where n=100 and R is:

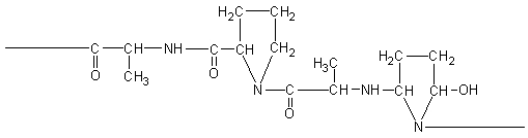


Fig.1 Formation of end product

Chemicals and materials

Hydrolyzate of collagen was industrially produced from chrome-tanning shavings by enzymatic hydrolysis (Brinckmann 2005). Shavings are mixed with fivefold amount of water and this mixture is alkalinized by using organic base together with magnesium hydroxide. After achievement uniform alkalinity of shavings, the mixture is heated up to 70°C. In one hour, 0.02 % of proteolytic enzyme is added and reaction is kept running at 70 °C for 2 – 4 hours. After that, heterogeneous mixture if filtered through vacuum filter and then the filtrate is vacuum-evaporated as long as the solids concentration is 30 – 40 %.

Mathematical model

Let us consider batch reactor, where components A and B react to each other. As a result this reaction, components C, D and E originate. Mentioned reaction system is possible to quantitatively express by mathematical notation:

$$-\frac{dc_A}{d\tau} = k_1 c_A c_B + k_3 (c_A)^2 \quad (4)$$

$$-\frac{dc_B}{d\tau} = k_1 c_A c_B \quad (5)$$

$$\frac{dc_C}{d\tau} = k_1 c_A c_B - k_2 c_C \quad (6)$$

$$\frac{dc_D}{d\tau} = k_2 c_C \quad (7)$$

$$\frac{dc_E}{d\tau} = k_3 (c_A)^2 \quad (8)$$

where τ[s] is time, c_X [mol] is concentration of substance X, k_1 [s^{-1}mol^{-1}], k_2 [s^{-1}] and k_3 [s^{-1}mol^{-1}] are velocity constants. Their values are unknown and have to be estimated or determined experimentally. Let us assume these initial conditions:

$$c_A(0) = 1 \quad c_B(0) = 1 \quad c_{AB}(0) = 0$$
$$c_C(0) = 1 \quad c_E(0) = 0$$

At the beginning of reaction, it is supposed equivalent amount of components A and B and the rest is equal to zero. Analysis of the system was examined by numerical solving of the mathematical model. Standard Runge-Kutta's method was successfully used.

Results

Parameters k_1, k_2, k_3 in the model were set on the basis of some experimental measurements and experience. At this

time, there are few various measurements which are focused on study of reaction course. For example, dielectric spectroscopy method measures change of dissipation factor (conductivity) or spectroscopy measurement follows the change in coloration of the product. Unknown parameters are derived from this preliminary measurement. In Fig. 2, an ideal case for manufacturing of final product is shown. Formation of aldol resins is almost extinguished (k3=0.001). The change of concentration of protein and glutaraldehyde is practically the same. On the contrary, in Fig. 3, a real process is demonstrated. Coefficient k3 is equal to 0.01 and end product is little coloured due to aldol resins. In practice, there is a need to reduce k3 as much as possible by suitable change of pH, for example.

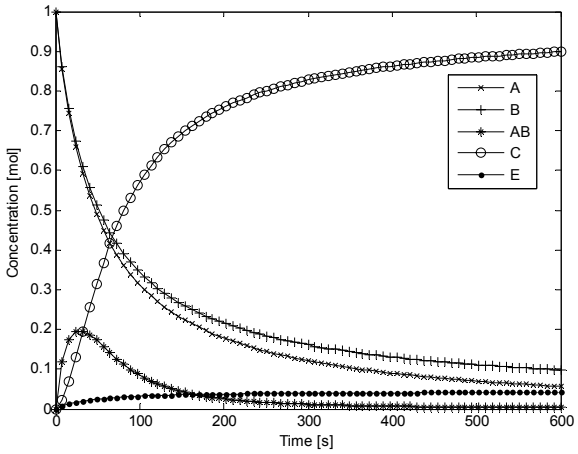


Fig.2 Simulation of the system with parameters k1=0.02; k2=0.04; k3=0.001;

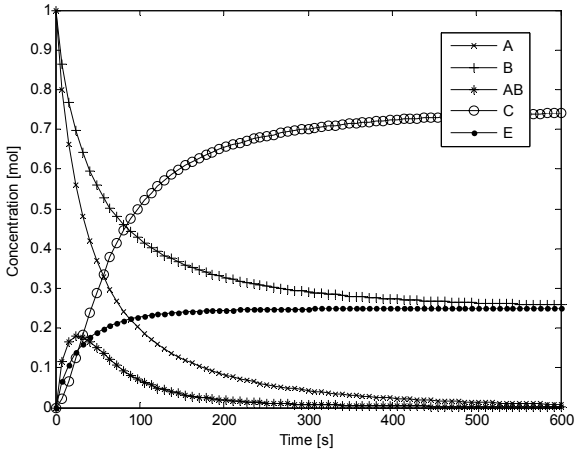


Fig.3 Simulation of the system with parameters k1=0.02; k2=0.04; k3=0.01;

Conclusion

Raw leather processing in tanning industry or collagen material in nutritional industry carries many technologically demanding procedures which results in production of various industrial waste besides final product. The chemical reaction between collagen material and cross-linking agent is cardinal operation. Its course is influenced by many factors and finally has an impact on final product. Key problem is a selection of any suitable measurable quantity. This sensory system can inform actuator of reaction state or kinetics conditions. As a result it allows execution of actions in individual technological steps. Mentioned problem can be solved by two different ways, which is a consequence of literature study. The former is concentrated on structure and texture of natural polymer from macromolecular chemistry point of view. The latter exploits mathematical-statistical processing of experimental data or data measured in industrial process. The purpose of this is finding of predominant factors on investigated target function. Nowadays, a fully automatic control of cross-linking process is practically the only possibility. Simulation is necessary step before control design of this system.

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