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ISNI: 0000 0004 8495 2390

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JOURNAL	World Science
p-ISSN	2413-1032
e-ISSN	2414-6404
PUBLISHER	RS Global Sp. z O.O., Poland

ARTICLE TITLE	STUDY OF POLYCONDENSATION PROCESS OF CARBAMIDE WITH FORMALDEHYDE TO RECEIVE BIODEGRADABLE POLYMERS
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ARTICLE INFO	Givi Papava, Nazi Gelashvili, Eter Gavashelidze, Riva Liparteliani, Ketevan Archvadze. (2020) Study of Polycondensation Process of Carbamide with Formaldehyde to Receive Biodegradable Polymers. World Science. 7(59). doi: 10.31435/rsglobal_ws/30092020/7209
DOI	https://doi.org/10.31435/rsglobal_ws/30092020/7209
RECEIVED	14 July 2020
ACCEPTED	29 August 2020
PUBLISHED	04 September 2020
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STUDY OF POLYCONDENSATION PROCESS OF CARBAMIDE WITH FORMALDEHYDE TO RECEIVE BIODEGRADABLE POLYMERS

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DOI: https://doi.org/10.31435/rsglobal_ws/30092020/7209

ARTICLE INFO

Received: 14 July 2020
Accepted: 29 August 2020
Published: 04 September 2020

KEYWORDS

spatial structure,
linear structure,
peptide bond,
microorganisms,
biodegradable,
prolonged action,
synthesis,
temperature,
duration,
catalyst.

ABSTRACT

Biodegradation of polymers of spatial structure is complicated at the impact of soil destructive microorganisms and biodegradation requires long time. We have implemented target-oriented synthesis of a polymer to receive linear structure polymers where labile peptide bonds are preserved.
To implement target-oriented synthesis of a polymer and to determine optimal conditions for reaction mechanism we studied the process of kinetics and its regularities – reaction temperature, duration, components ratio, concentration, reaction speed constant and activation energy. The Arrhenius factor and succession of introduction of initial components to the reaction medium were computed, catalyst nature and other properties were determined.
High effect of prolongation was achieved, when carbamide and formaldehyde molar ratio was 1:1. In this case linear structure polymer is formed where peptide $–CH_2 – NH –$ are preserved.
The simplified structure of linear polymer is expressed as followed: $–HNCONHCH_2[\ NHCONHCH_2\ ]_n – HNCONHCH_2 –$.

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Intense growth of the population requires increase of agricultural products, especially of cereal crops but agricultural designation lands suffer constant decrease thanks to the increased urbanization and intensification of industry. The only way to provide the population with farm products is application of nitrogen-containing chemical fertilizers in increased doses (mainly of ammonium nitrate and carbamide). But due to good water solubility of nitrogenous fertilizers their significant part is lost as a result of evaporation and wash-off. Alongside with tremendous economic loss it results in global environment contamination and creates heavy ecological conditions for normal existence of population and fauna.

Regular application of such fertilizers makes unfavorable impact on soil and environment (1-3). It can condition misbalance of nutrients used by plants, while accumulation of nitrates in great quantity negatively affects human and animal health (4-5).

Efficient way to resolve these problems was creation of absolutely new type fertilizers, the so-called "exchange fertilizers", which were developed in USA, by the Geological Service (6).

Principle of the application of exchange fertilizer differs cardinally from that of commonly used fertilizers, which are well soluble in ground waters and are easily washed off. Exchange fertilizers consist of hardly soluble ingredients which are released as plant nutrient components and are consumed by plants according to need, due to buffer effect of chemical reactions going on in soil.

The system offered by us is based on the principle that natural ion-exchangers, e.g. zeolites are able to add calcium ion released from Apatite, which is goes on till complete dissolution of Apatite (8,9). The simplified scheme for this system is as follows:

$$\text{P-Apatite} + (NH_4, K)\text{-zeolite} = \text{Ca-zeolite} + (NH_4^+, K^+) + H_2PO_4^-$$

Exchange fertilizers are highly efficient for assimilation of nutrients by plants, thus helping plants to assimilate nutrients more efficiently and to decrease washing-off the nutrients and environment pollution.

At the application of exchange fertilizers productivity is increased compared to that when common soluble fertilizers are used. (www.zeoponic.com).Thus, for example Barbarick and his collaborators (7) proved that productivity of sorgurum-sudangrass in some systems was increased by 4 factors. One of the modifications of this fertilizer was commercialized by Zeoponic Inc (see www.zeoponic.com) and was spread worldwide. Irrespective of these positive results the exchange fertilizers are not perfect for wide application in agriculture. The main problem is that it doesn't contain much nitrogen (it contains approximately 2.5 mass%) in the form of ammonium ion in zeolite acting in exchange process (NH_4- form of zeolite).

Development of ecologically safe fertilizers is attributed vital significance for our survival.

The submitted project enables us to develop such fertilizers.

Among the nitrogenous fertilizers mainly ammonium nitrate (NH_4NO_3) and carbamide (H_2N-CO-NH_2) are used in agriculture. Carbamide contains up to 46% nitrogen, while nitrate – 35%. But both of them are rather well soluble in water. While introducing into soil their significant part is easily and swiftly washed off at the impact of ground and rain waters, which results in tremendous economic loss, contamination of environment (water reservoirs, lakes, seas, ponds, wells and heavy diseases in the population and animals. At the same time, as a result of evaporation, while reaching the high strata of atmosphere it results in destruction of ozone layer that protects the globe.

According to our opinion one of the efficient ways to overcome these problems is application of polymer fertilizers which are hardly soluble in water. When introduced into soil, at the impact of destructive microorganisms the fertilizer suffers conversion and passes into the form easily assimilated by plants. This process proceeds slowly and a plant manages its assimilation. At the same time, in the vegetation period a plant is provided with dosed and (in case of capsulation) autonomous feeding and it is developed normally, which is a prerequisite of obtaining ecologically pure product and increase of productivity.

Biodegradation of spatial polymer at the impact of destructive microorganisms of soil is complicated and requires a long time. We have implemented a target-oriented synthesis of polymers to receive linear structure polymers where labile peptide bonds are preserved. To realize target-oriented synthesis of polymers and to determine reaction mechanism and optimal conditions of synthesis we studied the process kinetics and reaction regularities.

Some kinetic regularities of interaction of amide component and aldehyde were studied when the reaction was carried out in the solution at 50-70°C at carbamide/formaldehyde molar ration 1:2, correspondingly.

Various factors affect the process of carbamide and formaldehyde interaction reaction. These are: process duration, temperature, molar ratio of starting components, amide component structure and composition, concentration of the solution. At the increase of temperature, conversion rate and reaction speed are increased. Thus, for example, after 15 minutes, conversion level at 50°C reaches 29.23%, at 60°C − 43.58% while at 70°C it reaches 71.79%. Besides the reaction length makes influence on the conversion level. Conversion level increases together with the reaction duration. Practically, reaction is completed in one hour.

We studied the effect of carbamide and formaldehyde ratio on the reaction process. At the increase of formaldehyde quantity, conversion level and speed increase markedly. Already after one minute of the reaction carbamide-formaldehyde ratio equals to 1:2 mol and conversion rate is 5%. At the increase of this ratio up to 1:4, conversion level after 30 minutes increases from 60 to 77%.

Some kinetic regularities of the interaction of amide components and aldehyde in the solution were studied at constant temperature, at 50, 60 and 70°C, when carbamide/formaldehyde ratio was 1:2. It was shown that reaction speed was increased with the increase of temperature and duration. 1-3 tables show kinetic parameters when the reaction was carried out at 50, 60 and 70°C:

Table 1. Kinetic parameters at the reaction carried out at 50°C x)

t, min	x	a -x	a(a - x)	a(a -x)t	K, l/mol.sec.	P, %
1	0,00053	0,001892	$3,6991 \cdot 10^{-6}$	$3,2194 \cdot 10^{-4}$	$2,3884 \cdot 10^{-1}$	2,71
3	0,00015	0,00180	$3,5100 \cdot 10^{-6}$	$6,3180 \cdot 10^{-4}$	$2,3741 \cdot 10^{-1}$	7,69
5	0,00024	0,00171	$3,3345 \cdot 10^{-6}$	$10,0035 \cdot 10^{-4}$	$2,3900 \cdot 10^{-1}$	12,30
10	0,00042	0,00153	$3,9835 \cdot 10^{-6}$	$17,9000 \cdot 10^{-4}$	$2,3463 \cdot 10^{-1}$	21,53
15	0,00057	0,00138	$3,6910 \cdot 10^{-6}$	$24,2190 \cdot 10^{-4}$	$2,3535 \cdot 10^{-1}$	29,23
20	0,00069	0,00126	$3,4570 \cdot 10^{-6}$	$29,4840 \cdot 10^{-4}$	$2,3402 \cdot 10^{-1}$	35,38
25	0,0008	0,00115	$3,2425 \cdot 10^{-6}$	$33,6375 \cdot 10^{-4}$	$2,37,83 \cdot 10^{-1}$	41,02
30	0,00088	0,00107	$3,0865 \cdot 10^{-6}$	$37,5570 \cdot 10^{-4}$	$2,3431 \cdot 10^{-1}$	45,12
45	0,00108	0,00087	$3,6965 \cdot 10^{-6}$	$45,8055 \cdot 10^{-4}$	$2,3578 \cdot 10^{-1}$	55,38
60	0,00122	0,00073	$3,4235 \cdot 10^{-6}$	$51,2460 \cdot 10^{-4}$	$2,3806 \cdot 10^{-1}$	62,56
					aver. $2,3652 \cdot 10^{-1}$	

Table 2. Kinetic parameters at the reaction carried out at 60°C x)

t, min	x	a -x	a(a - x)	a(a -x)t	K, l/mol.sec.	P, %
1	0,0001	0,00185	$3,6075 \cdot 10^{-6}$	$2,1645 \cdot 10^{-4}$	$4,6210 \cdot 10^{-1}$	5,12
3	0,00026	0,00169	$3,2955 \cdot 10^{-6}$	$5,9319 \cdot 10^{-4}$	$4,3837 \cdot 10^{-1}$	13,33
5	0,0004	0,00155	$3,0225 \cdot 10^{-6}$	$9,0675 \cdot 10^{-4}$	$4,4116 \cdot 10^{-1}$	20,51
10	0,00066	0,00129	$2,5155 \cdot 10^{-6}$	$15,0930 \cdot 10^{-4}$	$4,3728 \cdot 10^{-1}$	38,84
15	0,00085	0,0011	$2,1450 \cdot 10^{-6}$	$19,3050 \cdot 10^{-4}$	$4,4030 \cdot 10^{-1}$	48,58
20	0,00099	0,00096	$1,8720 \cdot 10^{-6}$	$22,4640 \cdot 10^{-4}$	$4,4076 \cdot 10^{-1}$	50,76
25	0,00109	0,00086	$1,6770 \cdot 10^{-6}$	$25,1550 \cdot 10^{-4}$	$4,3831 \cdot 10^{-1}$	55,89
30	0,00118	0,00077	$1,5015 \cdot 10^{-6}$	$27,0227 \cdot 10^{-4}$	$4,3660 \cdot 10^{-1}$	60,51
45	0,00136	0,00059	$1,1505 \cdot 10^{-6}$	$31,0635 \cdot 10^{-4}$	$4,3781 \cdot 10^{-1}$	69,74
60	0,00147	0,00048	$9,3600 \cdot 10^{-7}$	$33,6960 \cdot 10^{-4}$	$4,3625 \cdot 10^{-1}$	75,38
					aver. $4,4038 \cdot 10^{-1}$	

Table 3. Kinetic parameters at the reaction carried out at 70°C x)

t, min	x	a -x	a(a - x)	a(a -x)t	K, l/mol.sec	P, %
1	0,00028	0,00167	$3,2565 \cdot 10^{-6}$	$1,9539 \cdot 10^{-4}$	$14,3369 \cdot 10^{-1}$	5,12
3	0,00065	0,0013	$2,5350 \cdot 10^{-6}$	$4,5630 \cdot 10^{-4}$	$14,2450 \cdot 10^{-1}$	13,33
5	0,00089	0,00106	$2,0670 \cdot 10^{-6}$	$6,2010 \cdot 10^{-4}$	$14,3525 \cdot 10^{-1}$	20,51
10	0,00122	0,00073	$1,4235 \cdot 10^{-6}$	$8,5410 \cdot 10^{-4}$	$14,2840 \cdot 10^{-1}$	38,84
15	0,0014	0,00055	$1,0725 \cdot 10^{-6}$	$9,6525 \cdot 10^{-4}$	$14,5047 \cdot 10^{-1}$	48,58
20	0,0015	0,00045	$8,7750 \cdot 10^{-7}$	$10,5300 \cdot 10^{-4}$	$14,2450 \cdot 10^{-1}$	50,76
25	0,00158	0,00032	$7,2150 \cdot 10^{-7}$	$10,8225 \cdot 10^{-4}$	$14,5900 \cdot 10^{-1}$	55,89
30	0,00163	0,00032	$6,2400 \cdot 10^{-7}$	$11,2320 \cdot 10^{-4}$	$14,5121 \cdot 10^{-1}$	60,51
					aver. $14,3837 \cdot 10^{-1}$	

x) t –time in minutes, a-formaldehyde content in grams, at 100% conversion; x-formaldehyde quantity in grams, which is converted at this moment.

According to the Arrhenius formula number of molecules reacting in one second equals to a number of molecules attacking in one second multiplied by $e^{-\frac{E}{RT}}$, that is $K = A \cdot e^{-\frac{E}{RT}}$, from it $lgK = lgA - \frac{E}{4,57T}$, where K is reaction speed constant, E-reaction activation energy, A- Arrhenius factor.

Volumes of reaction activation energy and probability factor are computed and E average = 7940.05 cal/mol = 7.94 kcal.mol. A = 0.0223 cal.mol*10 ^{2} l/mol.sec.

Effect of various factors, such as initial components molar ratio, amide component structure and composition, concentration was studied on the reaction of carbamide/formaldehyde interaction reaction. Reaction process is affected also by initial concentration of components. It is shown that increase of initial concentration of carbamide in reaction medium from 0.1 to 5 mol/l, increases reaction speed and conversion level. Thus, e.g. when initial concentration of carbamide is 0.1 mol/l, after 1 hour conversion level equals to 62.50%, when initial concentration is 1 mol/l – it is 66%, but when this concentration is 5 mol/l – conversion level equals to 78%.

The sequence of introduction of the initial components in the reaction area was studied. Carbamide is a multifunctional component and in case of simultaneous application of the initial components, a polymer with a spatial structure may be formed. When the aldehyde is gradually introduced into the reaction area the probability of reaction of aldehyde with the secondary hydrogen atom decreases, affecting the spatial structure of the polymer. When aldehyde is gradually introduced into the reaction area, there is always an excess of urea and the likelihood of the aldehyde reacting with the secondary hydrogen atom decreases.

It has been shown that by the increase of the initial concentration of aldehyde, the reaction rate increases.

The molar ratio of the initial components − carbamide and formaldehyde − greatly determines the chemical structure of the polymer obtained. When the molar ratio of the initial components − carbamide and formaldehyde is 1: 1,5-3,5, even when the pH is reduced to 4–4,5, it is possible to form a polymer with a spatial structure, which is highly undesirable for its use as a plastic material (due to poor flow which makes difficult its thermal treatment, it is also undesirable to use it as a fertilizer of prolonged action, since the period of adaptation and, consequently, that of biodegradation for degrading microorganisms is prolonged.

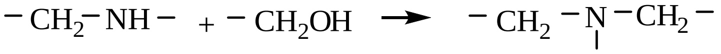
At such a ratio, methyl derivatives (mono-, di- and trimethyl derivatives) are formed at the initial stage of the reaction. Methylol groups are characterized by unstable and high reactivity. In the post-reaction phase, reactions may occur when the methylol group will react with the urea-free NH_2 group.

$$-CH_2OH + -NH_2 \rightarrow -CH_2 - NH -$$

Methylol groups interact with each other to form a dimethylene ether group, which then disintegrates.

$$-CH_2OH + -CH_2OH - CH_2 - O - CH_2 - \rightarrow -CH_2 -) + CH_2O$$

The methylol group interacts with the imine group. At this time a spatial structure is formed



$$-CH_2-NH- \; + \; -CH_2OH \longrightarrow -CH_2-\underset{|}{N}-CH_2-$$

As studies have shown, a high prolongation effect is achieved when the molar ratio of urea and formaldehyde is 1: 1. At this time a linear structure polymer is formed in which the peptide bonds $-CH_2 - NH -$ are retained.

The simplified structure of the linear polymer is expressed as follows:

$$- HNCONHCH_2[\ NHCONHCH_2\ ]_n - HNCONHCH_2 -$$

A study of the nature of the catalyst has shown that strong acids, such as sulfuric acid, hydrochloric acid, and phosphoric acid, accelerate the process much faster than formic or boric acids.

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