ZBIGNIEW K. BRZOZOWSKI

STARCH – ACRYLAMIDE COPOLYMERS

Abstract

Potato starch was modified by acrylamide under basic condition either via polyaddition or in acidic media via graft copolymeryzation.

Modified starch was applied as environmentally friendly agent for the following purposes: a formaldehyde scavenger from formaldehyde resins especially urea-formaldehyde resins used in chipboards or phenol-formaldehyde resins for binding of insulation mineral fiber-plates; agents reducing drag flow in pipelines for waste liquids, and reinforcement of drillings in oil and gas mines.

Elaborated method of production of formaldehyde emission decreasing agents is wasteless. Starch/acrylamide copolymer is completely harmless and nontoxic product, useful for environmental protection.

Introduction

Availability, low price, simple modification, atoxicity, simple degradation, possibility of different application are advantages of natural polymers and their derivations. Potato starch was modified either by 1-chloro-2,3- propanodiol and acryloamide in basic conditions or in acidic media by graft copolymeryzation of acryloamide. Modified starch (MS) was applied as environmental friendly agents to play a role of:

1) formaldehyde scavenger from formaldehyde resins used in urea-formaldehyde chipboards or phenol-formaldehyde resins used for binding of insulation mineral fiber-plates,
2) agents reducing drag flow in pipelines for liquid waste,
3) drilling muds.

Formaldehyde

Formaldehyde vapours are highly toxic. In man, irritant effects to nose, throat, lung and eyes could be seen on exposure of ≥ 0.5 mg/m^3 with acute effect at 10 mg/m^3.

Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662Warszawa, Poland, tel. (+48) (+22) 621-44-39, fax (+48) (+22) 622-39-99, E-mail Zbigbi@ch.pw. edu.pl.

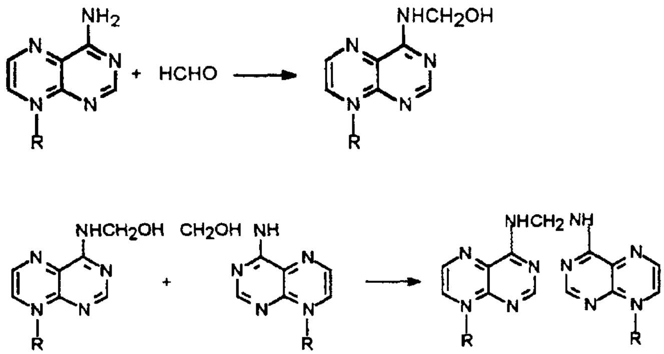


Fig. 1. Formation od DNA cross-links by formaldehyde.

In man, cutaneous sensitisation and allergic contact dermatitis have been well documented in individuals chronically exposed to formaldehyde – containing materials. A 2 % solution, however, does not produce acute skin irritant effects in man.

Formalin solution (26 %) has been shown to be severely irritant, producing permanent corneal injury in rabbits, guinea pigs and man. Splashes of a 4 % formaldehyde solution are highly irritant in man but no permanent effects have been reported.

A high reactivity of formaldehyde results in the formation of metylene cross-links between metylol groups by a condensation reaction between nucleotides of DNA in a single strand configuration as shown in Fig. 1.

These and other biochemical reactions have led to the expectation of genotoxic potential of formaldehyde and hence potential for carcinogenicity

The standards concerning the amount of formaldehyde in chipboard or plywood are still tightening. This trend is shown in Table 1.

Table 1

Trends in formaldehyde regulation

Period of time	Maximum formaldehyde content (mg/100g chipboard or plywood)
to 1970	100
1971-1973	65
1974-1975	45
1976-1977	30
1978-1981	25
1981-1986	20
1987-1990	> 10
1991-	>5

Modified starches (MS)

We investigated the modification of starch under acidic or basic conditions. The reaction of starch with acrylamide is shown below:

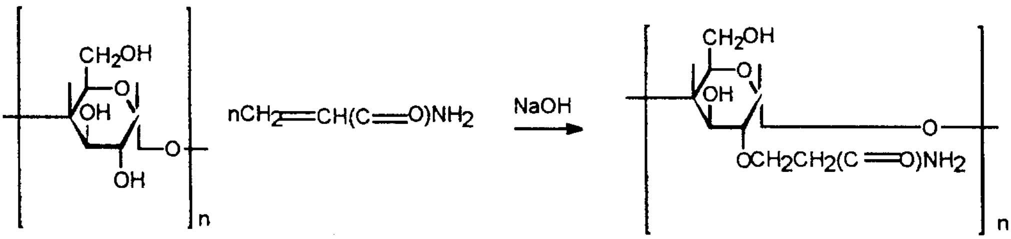


Fig. 2. Starch modification by acrylamide (S+AA).

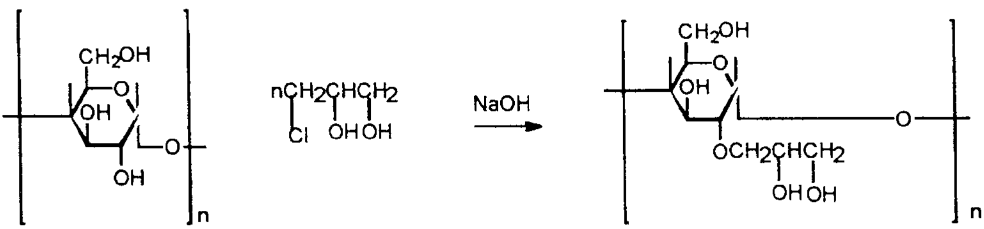


Fig. 3. Starch modification by chloropropandiol (S+CPD).

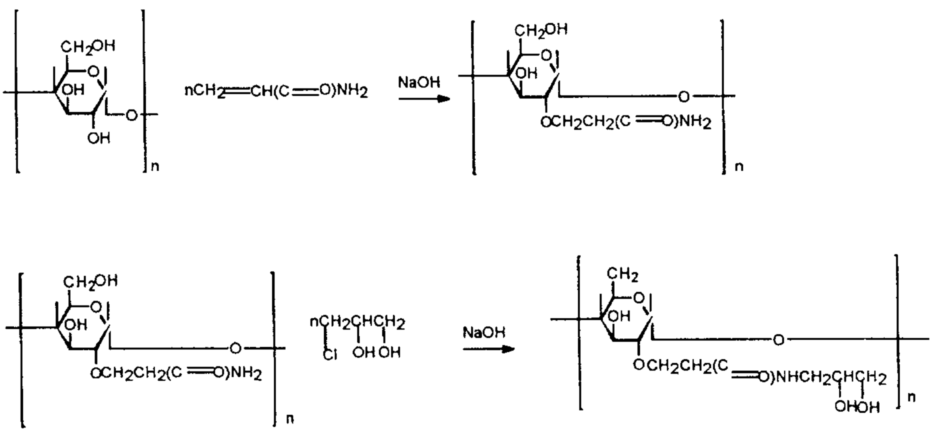


Fig. 4. Starch modification by acrylamide and chloropropandiol (S+AA+CPD).

Starch modification by the graft copolymerization with acryloamide.

Initiation

Me^{n+} + St–OH – Complex – St–O• + $Me^{(n-1)-}$ + H^+

St–O + M – St•–OM

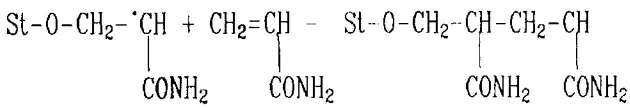
Polymerisation of acrylamide may proceed at the same time:

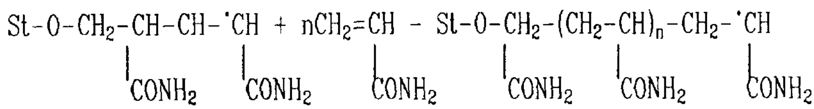
Me^{n+} + M–M• + $Me^{(n-1)-}$ + H^+

M + M• – M–M•

Chain extension

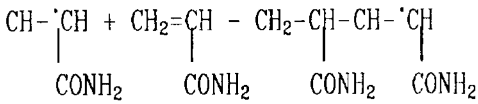
St–OM• + nM – St–OM–$(M)_{n+1}$M•

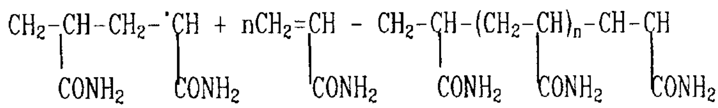




Chain extension of homopolimer is simultaneously formed.

M–M• + nM–$(M)_n$–M





Chain termination takes place as below:

St–O–M–(M)n–M• + Me^n – St–O–M–$(M)_n$-M + $Me^{(n-1)}$ + H^+

M–$(M)_n$–M + Me^{n+} – M–$(M)_n$–M + $Me^{(n-1)+}$ + H^+

Fig. 5. Starch modification by acrylamide in acidic condition.

Formaldehyde scavengers

The copolymer obtained was applied in aqueous solution as an additive to urea-formaldehyde resins. Following the technical guidelines we propose some binders consisting of urea-formaldehyde resin, curing agent (NH_4Cl-ammonium chloride), pure starch, diammonium phosphate and our graft copolymer in aqueous solution as a modifying agent.

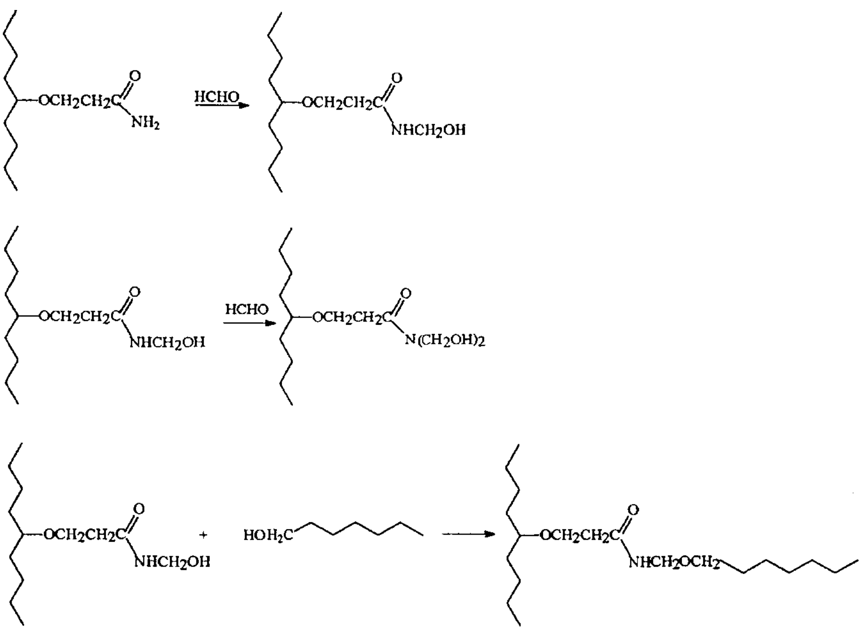


Fig. 6. The reaction of MS with formaldehyde occurs as follows:

We obtained chipboards using modifying agents with a free formaldehyde content below 10 mg per 100 g of chipboards (corresponding to E1 class for formaldehyde emission). These chipboards have the same physical and mechanical properties as chipboards prepared without a modifying agent. Thus, we eliminated about 58 % of the free formaldehyde emission, without altering the chipboards characteristics.

The Technical Chipboard Guidelines

1. The total content of dry substances in binding compounds $\geq 53\%$ should be maintained.
2. 4.5 g of 20 % aqueous solution of curing agent has to be added per 100 g urea-formaldehyde resin.
3. The time of binding compound gelation should be between 90 - 190 s.

The composition of a typical binding compound is given in Table 2.

The physical properties of the modifying agent used in this experiment are presented in Table 3.

Table 2

Typical binding compound composition.

Components	Quantity [g]	Dry substance [g]	Gelation time [s]	Dry substance [s]
Resin	100	66		
Modifying agent	10	0.69		
Starch	–	–	100	59.5
NH_4Cl	4.19	0.838		
$(NH_4)_2HPO_4$	1	1		

Table 3

Modifying agent properties.

Parameter	Modifying agent value
Density [g/cm^3]	1.145
Viscosity [mPa s]	122
Dry substance	6.55
pH	< 2
Miscibility with water	

Chipboards presses with modifying agents satisfy the requirements of Polish Standard BN-80/7123-04-03 for the highest quality of chipboard.

The physical properties of the chipboards which were bound with the modifying agent were identical to those of chipboards which were bound with pure urea-formaldehyde resins. The reduction of free formaldehyde emission in pressed chipboards were as follows:

Table 4

Reduction of free formaldehyde in chipboards

Case	Content of free formaldehyde (in mg/100g chipboards)
Without modifying agent	23.0
With modifying agent	9.7

We obtained chipboards using modifying agents with a free formaldehyde content below 10 mg per 100 g of chipboard (corresponding to E1 class for formaldehyde emission).

These chipboards have the same physical and mechanical properties as chipboards prepared without a modifying agent. We have thus eliminated about 58 % of free formaldehyde emission, without altering the chipboard characteristics.

Some properties of binding agents for chipboard before and after addition of MS are shown in Table 5.

Table 5

Chipboard properties and MS addition

Binding agent	Gelation time [s]	Emission of free formaldehyde [mg/100g]	Emission decrease [%]
Before MS addition	86	202	–
After MS addition	77	96	52

Formaldehyde scavengers based on modified starch have decreased the formaldehyde amount > 10 mg/100 g of chipboards or plywood without any depreciation of other properties.

Drag reduction of liquid flow

The special apparatus has been constructed for our laboratory investigations on the drag reduction of liquid flow – notably for the extraction of salt water from mines (Figure 7). The results are shown in Table 6.

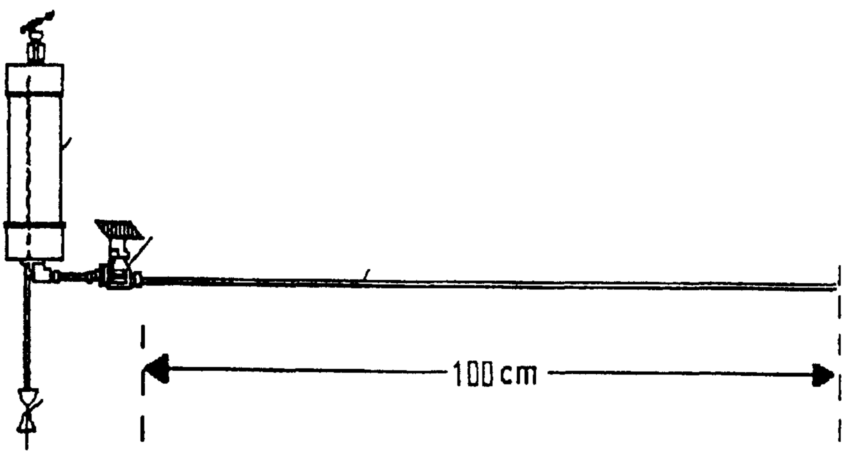


Fig. 7.

Table 6

(Density = 1026 kg/m^3, time = 34.2 sec.)

	Viscosity [m·Pa·s]	Mass [kg]	Re (Reynolds number)	Z (drag flow) [m]
Salt water	1.61	0.521	989	0.110
S+AA+CPD				
0.10 %	1.30	0.522	2453	0.060
0.8 %	1.37	0.526	2394	0.060
0.06 %	1.16	0.525	2815	0.050
0.04 %	1.14	0.527	2881	0.054
0.02 %	1.12	0.516	2850	0.051

The best results were obtained with the starch modified by acrylamide. Our products have identical reduction properties against drag flow as commercial products made by Allied Colloids.

Advantages of new modified natural polymers are as follows: availability, low price, simple modification, atoxicity, simple degradation, possibility of different application.

Elaborated production method of formaldehyde emission decreasing agents is wasteless. Starch/acrylamide copolymer is completely harmless and nontoxic for environmental protection and it evokes significant interest of environmentality.

REFERENCES

[1] Z.K. Brzozowski, K. Noniewicz: Polimery, **38** (1), 1993, 8.
[2] Z.K. Brzozowski, K. Noniewicz: Polimery, **38** (11-12), 1994, 726-730.
[3] K. Noniewicz, Z.K. Brzozowski, J. Mazur: Polimery, 39 (2), 1994, 82.

KOPOLIMERY SKROBIOWO-AKRYLOAMIDOWE

Streszczenie

Skrobię ziemniaczaną modyfikowano akryloamidem przez poliaddycję w środowisku zasadowym lub szczeponą kopolimeryzację w środowisku kwaśnym.

Skrobię modyfikowaną zastosowano jako czynnik bezpieczny dla środowiska naturalnego do następujących celów: wychwytywanie formaldehydu uwalnianego z żywic formaldehydowych, szczególnie żywic mocznikowo-formaldehydowych stosowanych do płyt wiórowych i żywic fenolowo-formaldehydowych do wiązania i izolowania elementów z włókien mineralnych, czynniki zmniejszające opory przepływu w rurociągach przesyłających ścieki oraz płuczki wiertnicze.

Opracowana metoda produkcji czynników zmniejszających emisję formaldehydu jest metodą bezodpadową. Kopolimer skrobi z akryloamidem jest zupełnie bezpieczny i nietoksyczny i nadaje się do zastosowania w działaniach chroniących środowisko naturalne.