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Starch-grafted-*N*-vinylformamide copolymers manufactured by reactive extrusion: synthesis and characterization

Summary — Potato starch grafted with *N*-vinylformamide (NVF) copolymers have been manufactured by reactive extrusion in presence of radical initiators: 2,2′-azobis(2-methylpropionamidine) dihydrogen chloride or 2,2′-azobis(isobutyronitrile). During extrusion the following parameters have been changed: screw speed, temperature profile and initiator type whereas constant weight ratio of the reaction components NVF/starch/water 40:100:34 was kept. Raw copolymerization products have been evaluated by solubility tests in alkali aqueous solution at pH 9.0. Contents of graft copolymer in raw copolymerization products have been determined on a basis of extraction with water/ethanol mixture in the ratio of 70:30. FT-IR spectra of starch-*g*-NVF copolymers have been recorded and polysaccharide chains were subjected to enzymatic degradation using α- and β-amylases. Residual poly(*N*-vinylformamide) (PNVF) chains were characterized *via* gel permeation chromatography. Molecular weights of grafted PNVF were compared with literature data of polyacrylamide chains grafted on potato starches.
Keywords: starch graft copolymer, reactive extrusion, *N*-vinylformamide.

KOPOLIMERY SZCZEPIONE *N*-WINYLOFORMAMIDU NA SKROBI ZIEMNIACZANEJ WYTWARZANE NA DRODZE WYTŁACZANIA REAKTYWNEGO: SYNTEZA I CHARAKTERYSTYKA

Streszczenie — W obecności inicjatorów rodnikowych: dichlorowodorku 2,2′-azobis(2-metylopropionamidyniowego) (AAPH) lub 2,2′-azobis(izobutyronitrylu) (AIBN) otrzymywano kopolimery szczepione *N*-winyloformamidu (NVF) na skrobi ziemniaczanej. W toku reaktywnego wytłaczania zmieniano szybkość obrotową ślimaków, profil temperaturowy (rys. 1) oraz rodzaj inicjatora, stały natomiast był stosunek masowy NVF/skrobia/woda 40:100:34. Badano rozpuszczalność w lekko alkalicznym roztworze wodnym (pH 9,0) surowych produktów kopolimeryzacji. Zawartość kopolimeru szczepionego w surowych kopolimerach określano na podstawie ekstrakcji mieszaniną woda/etanol (70:30) (tabela 1). Rejestrowano też widma FT-IR kopolimerów skrobia-*g*-NVF (rys. 2), a część polisacharydową kopolimerów poddano degradacji enzymatycznej za pomocą α- i β-amylaz. Pozostałe po degradacji enzymatycznej łańcuchy poli(*N*-winyloformamidowe) (PNVF) charakteryzowano metodą chromatografii żelowej (GPC) (rys. 3). Oznaczone wartości liczbowo średnich mas molowych naszczepionego PNVF porównywano z literaturowymi danymi dotyczącymi łańcuchów poliakryloamidu szczepionego na skrobi ziemniaczanej (tabela 2).
Słowa kluczowe: kopolimer szczepiony skrobi, reaktywne wytłaczanie, *N*-winyloformamid.

INTRODUCTION

Starch is naturally abundant polysaccharide and a low cost biodegradable material. Particular attention, especially in recent years, has been attached to synthesis of starch graft copolymers due to an increasing interest in new cost-effective polymers designated for various environmental and industrial applications. Hydrophilic graft starch copolymers, mainly bearing acrylamide branch units, are used in such areas as: water and waste-water treatment (flocculants [1, 2], sorbents of polyvalent metal cations [3, 4]), biodegradable superabsorbents [5, 6] (for hygienic and agrotechnical purposes, additives for cosmetics [7]), in paper industry (strengthening of paper [8]), textile industry (binders, fibre additives, preparations [9]), petrochemical and mineral recovery (mud components [10]).

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From application point of view starch graft copolymers with bonded hydrophilic chains composed of acrylamide (AAm) [11—13], acrylonitrile [11, 14, 15], acrylic acid (AA) [16, 17] or copolymers of AAm with anionic [5, 18, 19] or cationic [20, 21] monomers are the most important.

Starch-grafted copolymer synthesis is often performed by batch radical processes at low concentration of starch because of problem with efficient mixing after gelatinization. Such starch reactions use lot of water and energy. Graft copolymerization of starch performed by reactive extrusion usually in double-screw extruders brings some benefits such as elastic controlling of the process: adjustment of temperature profile along the extruder, screw speed, some freedom of coreagent dosage place and residence time in the extruder, and also general higher economy of the technological production process [22].

For starch graft copolymerization with AAm and/or other hydrophilic monomers the following chemical initiators are most often used: (i) cerium(IV) salts [*eg.* Ce(IV) ammonium nitrate], (ii) ammonium, sodium or potassium persulfates, and (iii) redox systems [*e.g.* Fe(II)/H_2O_2]. The first from the mentioned initiators, creates active radicals directly on polysaccharide chains, thus starch graft copolymer is formed exclusively. Other initiators cause formation of ungrafted homopolymers (or copolymers if mixtures of monomers are applied) besides the true graft copolymer. Willet and Finkenstadt [23] found that using of Ce(IV) salt for AAm grafting onto starch offers unsatisfactory parameters of grafting as compared to the other radical initiators. The following physicochemical parameters for Ce(IV) initiated copolymers were lower than those for persulfate or redox initiated copolymers: grafting efficiency 7—24 % versus 43—86 %, monomer conversion 7—16 % versus 73—99 %, amount of grafted branches 1—2.5 % versus 14—37 %; and also lower molecular weight of the grafted AAm branches [23].

The aim of this study was to investigate *N*-vinylformamide (NVF) graft copolymerization on starch during reactive extrusion. NVF is an isomer of AAm considered as environmentally safer in comparison with the latter which is known as mutagenic monomer. NVF is a highly reactive; that feature is not always positive because it can react into some nonpolymeric by-products [24]. Molecular weights of NVF polymers obtained in neutral environment (pH = 6—7) are generally lower than those of polyacrylamides [24, 25]. Mostafa *et al.* [26] recently described starch graft copolymerization with NVF (starch/monomer weight ratio 100/12.5—200) in conventional batch process while redox initiator bromate/cyclohexanone was used. At optimal reaction conditions (pH = 6, 40 °C, 120 min, 50 wt. % NVF in relation to starch) the product with yield 41 %, and grafting efficiency 81 % was obtained (21 wt. % of ungrafted polyNVF has been determined in the reaction product). The products exhibited degree of swelling and solubility in water in the range of 90—310 wt. % and 9.5—47.5 wt. %, respectively.

According to our knowledge, graft copolymerization of starch with NVF by reactive extrusion has not been yet described in literature.

In this work starch grafted with *N*-vinylformamide has been synthesized by reactive extrusion, and some physicochemical properties of the products have been investigated.

EXPERIMENTAL

Materials

Potato starch was supplied by Nowamyl S.A., Nowogard, Poland.

Monomer: *N*-vinylformamid (technical grade for synthesis, BASF), was used without any pretreatment.

Initiators: 2,2′-azobis(2-methylpropionamidine) dihydrogen chloride (97 %, Sigma-Aldrich) (AAPH) and 2,2′-azobis(isobutyronitrile) (pure for analysis, Acros Organic) (AIBN) were used as delivered.

Graft copolymerization

Starch grafting copolymerizations have been performed in laboratory double screw corotating extruder (Prism Eurolab 16, Thermo-Electron Corp., Great Britain), D = 16 mm, L/D = 40. Starch and all other components were introduced into the first zone of the extruder (Fig. 1). Temperature profiles of the heating zones of the extruder during graft copolymerization processes were kept in the range of 60—115 °C. Speed rotation of the screws was changed between 60 and 300 rpm. Amount of moisture in starch before processing was controlled using thermo-balance (WSP 110S, Radwag, Poland). The determined amount of water was taken into account in the final balance of water in the reaction system. Total amount of water was 34 wt. parts/100 wt. parts of dry starch. Weight ratio of monomer to starch was 40/100. Concentration of radical initiators, *i.e.* AAPH and AIBN was 1.0 wt. % in relation to dry starch.

Sample preparation for physicochemical characterization

Solubility tests in aqueous alkali solutions of the raw products of starch graft copolymerization were performed at pH 9.0. Other tests or measurements of the copolymers were carried out on „real" starch graft copolymers isolated from the raw reaction products after ungrafted homopolymer extraction with water/ethanol mixture in ratio of 70/30 by weight. For solubility test 1.0 g of ground raw copolymer (fraction below 0.5 mm) was introduced into 30 g distilled water and the system was mixed for 1 h. Before copolymer introduction in order to adjust the pH to 9 a few drops of 0.5 M aqueous

NaOH solution was added to the system. After that residual deposit was separated from the solution by filtration. Then the deposit was dried at 60 °C up to a constant mass.

Isolation of starch graft copolymers and their content determination in raw extrusion products

According to literature [12] water/ethanol mixture in ratio of 70/30 by weight dissolves ungrafted homopolymers of AAm or NVF. Starch graft copolymers are not soluble and stay as residual solids after the homopolymer extraction. However, some low molecular fraction of starch as well as starch-*g*-NVF copolymer may also dissolve [12, 13, 23].

For isolation and determination of graft starch copolymer content 1 g of ground raw copolymer (fraction below 0.5 mm) was introduced into Erlenmayer flask containing 30 g water/ethanol mixture (70/30 w/w) solution and mixed for 24 h. Residual deposit was filtered and dried at 60 °C up to a constant mass and ground before physicochemical characterization. Content of graft copolymer was determined in wt. %.

Enzymatic degradation of polysaccharide chain of the graft copolymer

In order to determine the length of grafted poly-NVF chains the selected starch graft copolymers have been enzymatically degraded using α-amylase from *Aspergillusoryzae* (A9857, Sigma) and potato β-amylase (A7005, Sigma) enzymes. As a result grafted branches PNVF have been preserved unchanged whereas polysaccharide parts of the copolymer degraded up to lower molecular weight of glucose derivatives.

Procedure of sample preparation and graft copolymer enzymatic degradation was as follows: 0.5 g ground graft copolymer (fraction below 0.5 mm) was disperged in 5 cm^3 cold distilled water and then heated up to boiling for 1—2 min. Next, the solution was cooled down and introduced 1.25 cm^3 acetate buffer solution (prepared by dissolution 41 g sodium acetate and 30 cm^3 acetic acid in 250 cm^3 distilled water). Then prepared sample solution was added into 25 cm^3 measuring flask which was then filled with water. The enzymatic degradation was performed according to the following procedure: (i) 1 cm^3 α-amylase solution (0.0025 g α-amylase dissolved in 25 cm^3 distilled water) was mixed with 1 cm^3 β-amylase solution (0.0125 g β-amylase dissolved in 25 cm^3 distilled water); (ii) 1 cm^3 of 1 % acetate buffer solution was added into prepared starch graft copolymer solution, (iii) final copolymer solution prepared according to (ii) was incubated in water bath at 30 °C for 10, 20 and 30 min, (iv) into graft copolymer solution after incubation 2 cm^3 reagent: 3,5-dinitrosalicylic acid heated earlier to boiling through 20 min was added, (v) sample solution was then heated to boiling for 5 min and rapidly cooled down by introducing 20 cm^3 cold distilled water, (vi) solutions after enzymatic degradation were frozen before using for gel permeation analysis.

Methods of testing

Gel permeation chromatography

To evaluate molecular parameters of enzymatic degradation products of starch graft copolymers gel permeation chromatography was applied. Shodex OHpak SB-806M MQ column and Shodex OHpak SB-G precolumn, Merck Hitachi Liquid Chromatograph (pump L-7100, interface D-7000) with RI detector (Merck Lachrom RI L-7490) have been used. Eluent: acetate buffer (0.5 M acetic acid + 0.5 M sodium acetate); flow rate 0.5 cm^3/min. Dextran standards were used for the column calibration.

Infrared spectroscopy

Infrared spectra for the starch/NVF copolymer were recorded using Fourier transform instrument, Nexus FT-IR fitted with Golden Gate attenuated total reflection (ATR) accessory (Thermo-Nicolet Corp., USA). Spectra were recorded by OMNIC software.

RESULTS AND DISCUSSION

In Table 1 two series of starch/NVF graft copolymers manufactured by reactive extrusion initiated with AAPH and AIBN are presented. In both cases 40 wt. parts of NVF per 100 wt. parts of starch, constant amount of water (34 wt. parts/100 wt. parts of starch) and initiator (1 wt. part/100 wt. parts of starch) have been used while screw rotation changed between 60 and 300 rpm (A—D letters in the sample symbols).

It may be seen that obtained raw starch copolymers exhibit solubility in aqueous slightly alkali solution (pH 9.0) in the range of *ca.* 18—43 %. Soluble components include: unreacted NVF, NVF homopolymer as well as part of starch-*g*-NVF copolymers. Range of solubility of the copolymerization products obtained with both initiators are similar (AAPH initiated: 20—43 wt. %, AIBN initiated: 18—38 wt. %). Higher values of this parameter are found for the raw copolymerization products manufactured at lower temperature profiles I and III operating at 60 °C on the first six heating zones of the extruder (see Fig. 1 and Table 1).

For comparison real batch-synthesized starch/NVF copolymer based on pregelled starch exhibited solubility in water *ca.* 33 wt. % for comparable NVF/starch weight ratio 37.5/100 and other initiating system [26].

In Table 1 data on starch graft copolymer contents in the reactive extrusion products are also presented. As it can be seen, graft copolymer contents varied between 50 and 75 wt. % being higher in case of AIBN initiated copolymers (58—75 wt. %) in comparison to these pro-

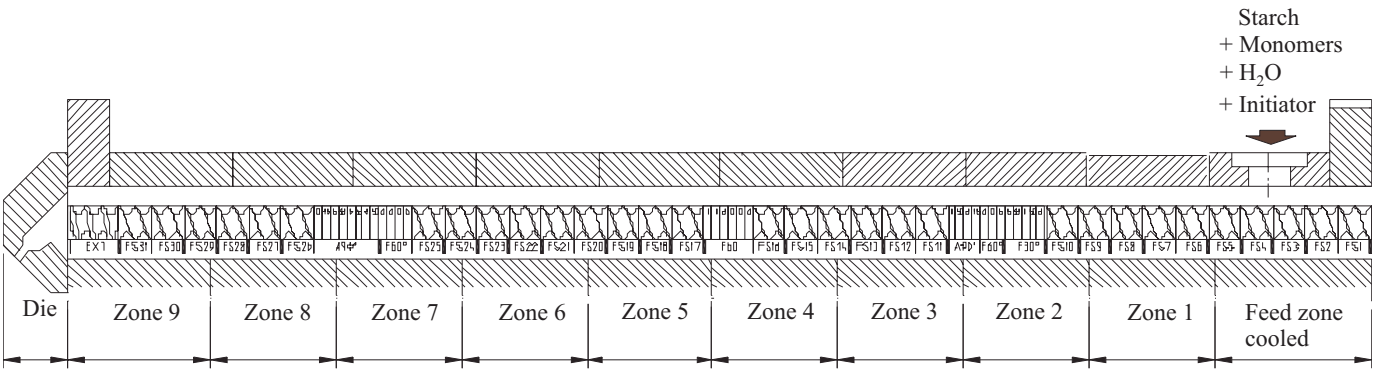

Fig. 1. Schematic view of the double-screw corotating extruder with marked zone of reagents feeting

T a b l e 1. Starch grafted with NVF in presence of various initiators

Component	Amount wt. parts	Sample acronym, respectively/ temperature profile*)	Solubility (pH 9.0), wt. %				Graft copolymer content, wt. %			
			rpm							
			60 (A)	100 (B)	200 (C)	300 (D)	60 (A)	100 (B)	200 (C)	300 (D)
NVF	40	AW11A-1/I; AW11B-1/I	43.0	39.1	—	—	55	54	—	—
Starch	100	AW11A-2/II; AW11B-2/II; AW11C-2/II	33.8	26.5	26.4	—	62	61	52	—
Water	34	AW14B-1/II; AW14C-1/II; AW14D-1/II	—	21.9	20.4	20.8	—	64	55	58
AAPH	1	AW14B-2/III; AW14C-2/III; AW14D-2/III	—	31.9	25.3	23.0	—	51	50	60
NVF	40	AW12A-1/I; AW12B-1/I; AW12C-1/I	27.0	33.1	20.4	—	71	75	65	—
Starch	100	AW12A-2/II; AW12B-2/II; AW12C-2/II	25.0	27.9	17.6	—	73	63	70	—
Water	34	AW13B-1/II; AW13C-1/II; AW13D-1/II	—	25.0	32.1	24.5	—	65	60	63
AIBN	1	AW13A-2/III; AW13B-2/III; AW13C-2/III; AW13D-2/III	38.0	27.2	28.3	31.4	—	61	61	58

*) Temperature profiles: I — 60/60/60/60/60/60/80/100/115/80 °C, II — 80/80/80/80/80/80/100/100/115/80 °C, III — 60/60/60/60/60/60/80/100/115/88 °C.

duced by AAPH initiation (50—64 wt. %). This can be explained by limited solubility of the former initiator in NVF/water mixture and possible higher efficiency of graft copolymerization of the monomer. AIBN dissolves fully in NVF monomer but not in water whereas AAPH is soluble in the monomer as well as in water. Relevant pairs of data for the products synthesized at similar temperature profiles are scattered rather in the range of few wt. % [with exception of larger scatter for samples manufactured at 100 rpm (AW12B-1/I and AW13A-2/III) and at 200 rpm (AW12C-2/II and AW13-C-1/II)].

Fig. 2 presents FT-IR spectra of the selected starch-*g*-NVF copolymer (sample AW12C-1) and for comparison PNVF (synthesized *via* solution batch method) as well as native potato starch. Characteristic bands introduced to the copolymer by NVF units can be observed in the following wavelengths: of 1230—1370 cm^{-1} characteristic for PNVF spectrum, 1540 cm^{-1} -NH bending (amide II); 1670 cm^{-1} -C=O stretching (amide I) and also distinct 1720 cm^{-1} -C=O carbonyl band of ester link as a consequence of possible free radical oxygenation of NVF in a presence of atmospheric oxygen [27] and then esterification with OH groups of the polysaccharide. Such a band is not present in FT-IR spectrum of PNVF. The mentioned IR bands qualitatively support a fact of starch/NVF graft copolymer formation.

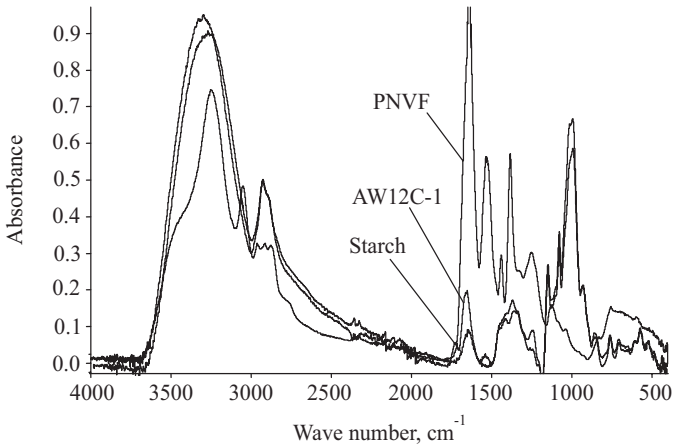

Fig. 2. FT-IR spectra for native starch, PNVF and starch grafted NVF (sample AW12C-1)

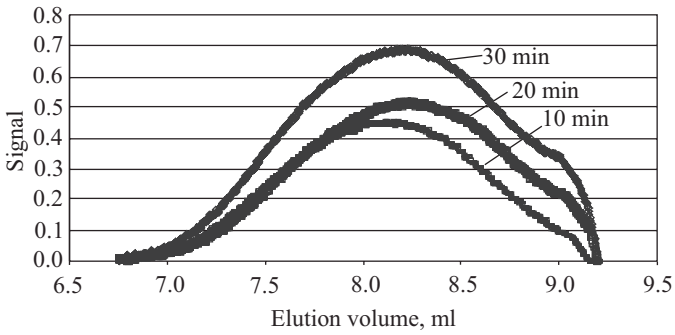

Fig. 3. GPC chromatograms of sample AW11B-2 after different time of enzymatic degradation

T a b l e 2. Number-average molar mass of poly(*N*-vinylformamide) chains after enzymatic degradation of polysaccharide part of starch/NVF graft copolymers

Copolymer description	Initiator type	Screw speed rpm	Enzymatic degradation time, min	M_n, g/mol
AW11A-2	AAPH	60	10, 20, 30	176 400; 285 000; 275 900
AW11B-2		100	10, 20, 30	247 100; 218 700; 265 300
AW11C-2		200	10, — , 30	231 800; — ; 201 000
AW12A-2	AIBN	60	10, 20, 30	185 400, 183 200; 194 200
AW12B-2		100	— , 20, 30	— , 276 900; 247 400

The applied enzymes, *i.e.* amylases belong to group of hydrolases splitting glycosidic bonds with water molecule inclusion. Real starch/NVF graft copolymers have been enzymatically degraded after 10, 20 and 30 min of incubation in water bath. After that products of enzymatic degradation were analyzed using GPC method to determine average molar mass of grafted PNVF chains as macromolecular residues of the starch grafted copolymer. High molar mass parts of GPC chromatograms have been registered (see Fig. 3 for sample AW11B-2 as an example). Number-average molar mass of PNVF chains unaltered during enzymatic degradation of polysaccharide chains of graft copolymers ranged from *ca.* 180 000 to 280 000 g/mol (Table 2). No clear dependence between PNVF chain lengths and experimental parameters of the reactive extrusion has been found (type of radical initiator, rpm of the extruder). These molecular data are lower than *M* values measured by Willet and Finkenstadt [12, 13] for polyacrylamide (PAAm) chains grafted on starch. Generally it may be expected that grafted chains of PNVF are shorter than those of PAAm because NVF monomer exhibits tendency to build up shorter chains in radical polymerization in comparison to AAm [24]. Starch-*g*-AAm copolymers manufactured by reactive extrusion of potato starch in experimental conditions different than used in this work (starch/AAm/water 100/50/50 by weight, ammonium persulfate 1 wt. %) exhibited *M* value *ca.* 550 000 g/mol for PAAm residue chains after enzymatic degradation with pullulanase and α-amylase [12]. Even higher *M* values were found for PAAm branches grafted on waxy maize starch or normal corn starch, *i.e.* 700 000 g/mol or higher. In another work of these authors [13] branches of PAAm obtained by reactive extrusion with lower weight ratio of regular corn starch 33/100 wt./wt. showed *M* value on a level 450 000 g/mol.

CONCLUSIONS

Series of potato starch/*N*-vinylformamide graft copolymers manufactured by reactive extrusion has been obtained and some their physicochemical properties were evaluated. The raw copolymerization products dissolve in slightly alkali solution (pH = 9.0) in the range of 18—43 wt. %; higher solubilities were found for the products obtained at lower extrusion temperature profile (six heating sections at 60 °C). Content of real graft copolymer in raw reactive products changes between 50 and 75 wt. %. FT-IR spectra have confirmed the presence of poly(*N*-vinylformamide) branches in the graft copolymers. Enzymatic degradation of starch-*g*-NVF copolymer using α-amylase/β-amylase enzyme system with the followed GPC analysis exhibited that grafted poly(*N*-vinylformamide) branches have number-average molar mass in the range of 180 000—280 000 g/mol, *i.e.* they are two-three times shorter than described in literature data for polyacrylamide branches of starch-*g*-acrylamide copolymers.

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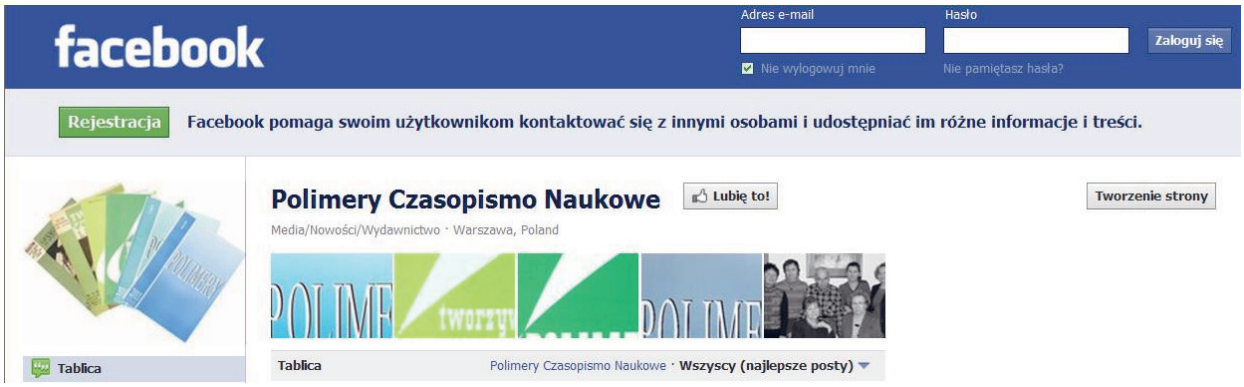

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