

Characterisation of Polacrylate-Polysaccharide System. Part I. Infrared Structural Studies

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Abstract

For the prepared polymer systems based on an poly(acrylic acid) and a colloidal solution of native starch, a series of IR (FTIR) structural studies and tests under heating conditions (ATR-FTIR) were carried out. Two components from the group of native starch of different biological origin (potato, cassava) were selected. The analysis of the collected results was aimed at assessing the effect of the biological origin of the starch on the structure, thermal sensitivity of the acrylic polymer-based system. On the basis of interaction effects occurring in the obtained synthetic polymer-natural polymer systems, the validity of mixing selected components to obtain composition was verified.

Keywords:

material engineering, hydrogel, native starch, polyacrylic acid, spectroscopy FT-IR

1. INTRODUCTION

Hydrogels are considered as a group of polymeric materials whose hydrophilic structure enables to retain large amounts of water in three-dimensional networks. Today, hydrogels continue to fascinate material scientists and researchers, and great progress has been made in their formulations and applications. The wide range of components, their mixability and origin mean that hydrogel materials are used in many industrial and environmental areas.

1.1. Hydrogels

A hydrogel is a gel in which the dispersed phase is water and the forming phase (gelling agent) may be a polymer – either natural (e.g. acacia gum, carrageenan, agar) or modified and synthetic (polysiloxanes, synthetic rubbers) [1, 2].

A number of methods for classifying hydrogels are encountered in the literature. Based on the type of interactions between the molecules that form the cross-linked gel structure, we distinguish between physical and chemical gels. In the latter, the macromolecules are linked to each other by covalent bonds, making these hydrogels usually thermally and chemically resistant. The structure of physical gels can be maintained by hydrogen bonds, molecular bonds, or ionic interactions. Under the influence of other substances, with a change in pH, or at elevated temperatures, physical gels can change to a sol state. This phenomenon is usually reversible. Depending on the chemical composition of the substance that forms the three-dimensional network, hydrogels are divided into organic and inorganic. Based on the source of the polymer that forms the solid phase, hydrogels

are classified into natural and synthetic. Another division of hydrogels involves the possession (or not) of an electrical charge in the polymer networks. Polymers that are ionisable or contain ionic groups are called polyelectrolytes. Among them we distinguish hydrogels: anionic (pectin, hyaluronic acid, alginic acid); cationic (chitosan, polylysine); amphoteric (starch, gelatine, collagen). They are also classified according to their structure, i.e. amorphous, which are formed due to the random linking of polymer chains, and semicrystalline, in which crystalline regions are present [3].

The properties of polymer hydrogels depend on many factors, including the type of polymer, the degree of cross-linking, the chemical composition of the liquid to be absorbed and also the fineness of the product (dispersed phase). Hydrogels can exist in a variety of physical forms including solids. The components used also determine the biocompatibility, non-toxicity, ability to absorb large quantities of water, flexibility, and chemical and thermal resistance that hydrogels usually possess [3]. Hydrogels are also characterised by their permeability, which is largely dependent on the porosity, size, distribution, and curvature of the pores. The more compact the hydrogel exhibits, the lower the permeability than the in the case of a broken down structure, i.e. larger pores, more pores.

As already indicated – hydrogels form a three-dimensional cross-linked structure. The polymer network (spatial structure) is formed due to the existence of chemical bonds between the polymer chains. This process is called chemical crosslinking. In a cross-linked hydrogel, we can distinguish between single covalent bond links, molecular entanglements and multifunctional links [3]. Crosslinking of polymeric hydrogels can be carried out by chemical and physical

methods. Chemical methods include crosslinking by radical polymerisation, chemical reaction of complementary groups, reaction with aldehydes, addition reaction, condensation reaction, by irradiation, using enzymes. Physical crosslinking methods occur by: ionic interaction, crystallisation, by the formation of stereocomplexes, by the formation of hydrogen bonds, by interaction with proteins [4].

New areas of material application are forcing innovative approaches in the design of hydrogels with much improved mechanical, sorptive, superporous properties and composed of chemically or even genetically modified components. Hydrogels, due to their diverse properties, are used in the chemical industry (for cosmetics), pharmaceutical industry (as wound plasters), biotechnology (replacing collagen, as contact lenses), food (for frozen food packaging), cosmetics (for soap production), metallurgy (heavy metal sorbents), as well as in environmental protection, agriculture and horticulture (agro-gels, soil-moisture granules) [4, 5].

It seems that there is a possibility to apply polymeric hydrogels also in casting, or rather mould technology. Namely, the application of this material can be related, for example, to obtaining models for moulds (or parts of their construction), as due to their properties they are interesting materials from the perspective of 3D printing technology [6, 7].

In simple terms, 3D printing technology using hydrogels involves applying thin layers of material in succession until the expected shape of the object is achieved. Advanced technologies make it possible to print a 'fibre' up to ten times thinner than a sheet of paper. This makes it possible to apply layers of material more precisely and to create complex and delicate forms, shapes (models). Literature data shows that parts printed from hydrogels are less brittle and more flexible. Moreover, after printing the desired shape, it is possible to subject the hydrogel object to drying, thanks to which water is removed from the object and the form itself visibly shrinks, while it returns to its original shape after soaking in water. Such properties are mainly used in medicine [7, 8].

Hydrogels are of interest based on both natural and synthetic components, with the latter gradually dominating the market with technological progress due to higher water absorption and long service life. The most popular synthetic base polymers of hydrogels are acrylic polymers, whose monomers of primary importance are acrylic acid, methacrylic acid, acrylamide, and their derivatives. Among natural polymers, polysaccharides and their modifiers are mentioned as components of hydrogels. In the case of this group of polymers, the type of biological raw material from which it is obtained may have a significant influence on its properties. In the following section, we discuss in more detail a polymer from the group of synthetic acrylic polymers: poly(acrylic acid) and a natural polymer: native starch.

1.2. Acrylic polymers – poly(acrylic acid)

Acrylic polymers are mainly obtained from the radical polymerisation reaction of acrylic acid, methacrylic acid or nitrile and amide ester derivatives. The monomer of the poly(acrylic acid) chains is acrylic acid – the simplest unsaturated carboxylic acid [1]. Poly(acrylic acid) is a weaker acid compared to its monomer. It shows solubility in polar compounds (water, lower alcohols, ethylene glycol), while it is insoluble in saturated and aromatic hydrocarbons. Solubility is reduced by an increase in molecular weight and increased by an increase in temperature. Poly(acrylic acid) is a polymer with high water-binding capacity and has hydrogel characteristics. Poly(acrylic acid) is most often used as an intermediate in the production of polymers used in many industries, e.g. automotive, construction, toys and paper. These plastics are used in the production of paints, adhesives, and adhesive tapes. They are used in dentistry, prosthetics, and orthopaedics as the basis for bone cement. In addition, the material can be used in the construction of hearing aids and the manufacture of contact lenses. It is also used as a thickening, dispersing and binding agent [9, 10]. Poly(acrylic acid) and its derivatives are also used in casting mould technology. They can be the main component of a casting binder, imparting strength to the mould, reducing the oscillation of moulding and core masses cured both chemically and physically. Finally, it acts as a binding and stabilising material in protective coatings [11–13].

1.3. Polysaccharide – native starch

Native (natural) starch is the most widespread polymer of the polysaccharide group in nature. It is found in potato tubers, flowers, stems, cereals, roots, and fruits. Its main function is as a storage element in plants – it stores energy, which, helps the plant to survive in difficult growth conditions (fluctuating temperature, drought). It is also a source of carbon (building material) for young germinating plants. There are two forms of starch in plant cells: storage starch and assimilatory starch. Assimilatory starch is synthesised in the leaves and is then broken down to sucrose, and sucrose itself is converted by biosynthesis to spare starch [14].

At the boundary between physical and chemical characteristics lies the ability of starch to gel (colloid). This process is related to the swelling of starch grains due to the action of water under higher temperature conditions (50–70°C). Solvent heating is necessary because native starch does not dissolve in cold water. When heated, the inter- and intramolecular hydrogen bonds of the starch components are broken. Water leaches out the amylose to form a colloid. The gelatinization of starch, the swelling and gelling process, the viscosity and stability of the gel depend on the origin (Table 1) and how the starch was extracted from the material [15].

Table 1
Example of gelatinisation temperature of starch of different botanical origin [15]

Starch type	Swelling onset temperature [°C]	Gelatinisation onset temperature [°C]	Full gelatinisation temperature [°C]
potato	46.0	59.0	62.5
wheat	50.0	65.0	67.5
rice	54.0	59.0	61.0
corn	50.0	55.0	62.5
cassava	49.0	58.0	63.0

As a result of gelatinisation, the crystallinity of the starch changes (semicrystalline to amorphous). Subsequently, during the storage period of the starch gel in amorphous form, the amylose molecules are organised by aggregation into a double helix through intermolecular hydrogen bonds. Such aggregates are secreted as dendrites and are insoluble in water. This process is called retrogradation. Its consequence is a reduction in the intermolecular spaces, which pushes water out of the gel (syneresis), which means dehydration of this material [15]. Retrogradation of starch colloids can occur over an extensive temperature range (-20°C to 100°C), but is most intense between -8°C and 8°C [16].

Because gel syneresis and retrogradation can cause the deterioration of food products, starches are subjected to various types of modification. The aim is to adapt the properties of the starch to the parameters of the technological process in order to produce a product with the desired shelf life, stability during application and storage. Among the physical methods of starch modification, a distinction is made between gelling, extrusion, agglomeration and combination methods [17]. Chemical modification processes are carried out by degradation of the polymer chain (hydrolysis, dextrination, oxidation), as well as by substitution reactions (esterification, etherification). The last and one of the most important methods of starch modification in the starch processing industry is crosslinking. This involves the replacement of weak hydrogen bonds with strong covalent bonds [18].

This paper presents a structural analysis of polyacrylic hydrogels with the addition of gelatinised native starch of different botanical origin (a combination of synthetic and natural polymers). A comparative analysis taking into account the influence of the botanical origin of starch on the hydrogel structure, including under elevated temperature conditions, has been carried out. The characterisation of the studied hydrogels will be useful in planning the technology of moulding objects in 3D printing technology.

2. EXPERIMENTAL

2.1. Materials

Based on literature data [19–21] poly(acrylic acid) (PA; PA80 – 35% aqueous solution/BASF) was selected for the preparation of polymer hydrogels. The polyacrylate hydrogel component was selected as:

- S_p – native (natural) potato starch (Trzemeszno S.A., Poland), white powder, odourless; moisture content 18.6%;
- S_c – native (natural) cassava starch (Cock Brand Marque Deposee, Thailand), white powder, odourless; moisture content of product 13.0%.

The solvent in hot-prepared colloidal solutions of natural starches – starch gels, was distilled water (Avantor Performance Materials Poland S.A.).

2.2. Samples natural starch solutions preparation

The preparation of PA+S hydrogels required the prior preparation of colloidal solutions of natural starches (starch gels). On

the basis of literature data [15]. The full gelatinization temperature of the potato and cassava starches was set at about 63°C . These data are relevant to the preparation of aqueous starch solutions.

A weighed portion of undried native starch in solid form (powder) was introduced into a glass vessel with cold distilled water at a weight ratio leading to a 10% solution. Then the whole was placed in a laboratory heating device with the power adjusted to reach the temperature of full gelatinisation of potato and cassava starch ($\sim 63^{\circ}\text{C}$). The temperature of the sample was controlled with a digital laboratory thermometer TH101.

For both types of starch, gelatinisation was carried out in an identical manner. The viscous solutions obtained were then directed to the preparation of polyacrylate hydrogels. Due to the possibility of the retrogradation process occurring during the storage of the colloidal starch solutions, the next steps of the study plan, i.e. the preparation of the systems with the acrylic polymer, were carried out within 2 h of the preparation of the gel.

2.3. Preparation of hydrogels

The experimental part of the paper focused on the study of two polyacrylate hydrogels based on polyacrylic acid water solution and gelatinised native starches (see Section 2.2). The ingredients ratio was: 1 parts by weight PA to 3.5 parts by weight starch gel. The hydrogels are designated in the text as follows:

- H-PA+S_p – PA-based polyacrylate hydrogel containing gelatinised potato starch (Fig. 1a);
- H-PA+S_c – PA-based polyacrylate hydrogel containing gelatinised cassava starch (Fig. 1b).

Approximately 1 g of H-PA+S_p and H-PA+S_c hydrogel was left in the conditioning chamber for 24 h at 25°C and 30–45% humidity to partially dry.

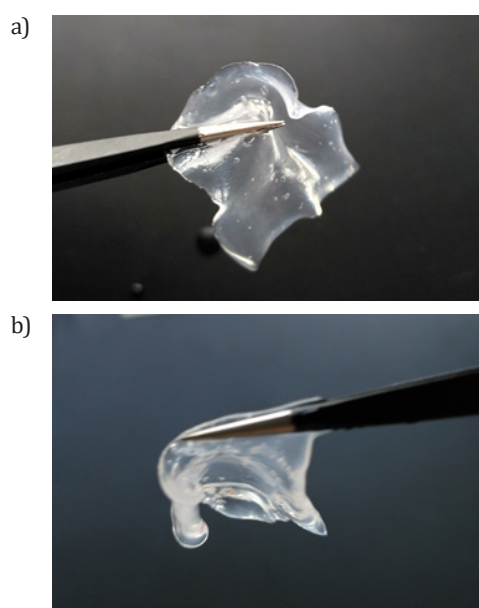


Fig. 1. View of a polyacrylate hydrogel object with starch after water adsorption: a) H-PA+S_p; b) H-PA+S_c

2.4. Methods

Fourier transform transmission spectroscopy

Recording of the spectra of the obtained hydrogels and their components was carried out as follows. The spectra were measured using the company's Digilab Excalibur FTS 3000 Mx Fourier spectrometer, in the range corresponding to mid-infrared. Two measurement techniques available to IR spectroscopy were used: transmission and reflection, using appropriate attachments.

In the Varian PRO software panel, the spectrum measurement parameters were established: wavenumber range 4000–400 cm^{-1} , spectral resolution of the apparatus 4 cm^{-1} , number of measurements to be averaged – 32 scans. Preparation of the KBr pellet started with weighing out 200 mg of potassium bromide KBr using an electric balance and grinding it in an agate mortar. KBr was then poured into a special matrix and pressed under 8 tonnes, using a hydraulic press. A pellet with a diameter of 10 mm and a thickness of about 1 mm was made. The resulting KBr pellet was placed in the spectrometer attachment and the background was measured. Next, another pastille was then prepared by weighing out 200 mg of KBr and adding about 2 mg of the test substance. The hydrogels and components investigated in this study have the consistency of a viscous liquid, so a small amount was applied directly to a pellet of pure potassium bromide. The pastille thus obtained as a sample carrier was placed in a spectrometer and the spectrum recorded.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

Studies of the effect of increasing temperature on the structure of the obtained hydrogels were carried out using the reflection multiple weakened reflection – the attenuated total reflection Fourier transform infra-red (ATR-FTIR) technique.

The temperature controller was set to an initial temperature of 25°C. In the Varian PRO software panel (which controls the operation of the Digilab Excalibur FTS 3000 Mx Fourier spectrometer), the following measurement parameters were set: wavenumber measurement range: 4000–600 cm^{-1} , spectral resolution of the instrument: 4 cm^{-1} , number of measurements to be averaged: 64 scans. After temperature stabilisation on the instrument, the background spectrum (air) was measured. The sample (1–2 mg) was placed with a Pasteur pipette on the appropriate surface of the attachment. The spectrum of the sample was recorded at 25°C and were repeated at 50°C, 75°C, 100°C, 125°C, 150°C, 175°C and 200°C, each time the temperature on the instrument was set by the controller; recording of the spectrum was initiated 30 s after reaching the set temperature on the instrument.

3. RESULTS AND DISCUSSION

3.1. Structural characteristics of polyacrylate hydrogels with natural starch

Figure 2 summarises the IR spectra of polyacrylate hydrogels and their components. Not only the liquid, freshly prepared hydrogel, but also the hydrogel dried in air for 24 h (in solid form) was tested.

The analysis of the FTIR spectra shows that natural potato starch and cassava starch in their initial form have a similar chemical structure. The maxima of the characteristic bands were located in a similar range of wave numbers, indicating that the same groupings are present in both samples. The difference in the shape of the spectra was located in the wavenumber range 3800–3000 cm^{-1} – two maxima on the S_p spectrum and one on the S_c spectrum – which may be related to the different proportion/proportion in the starch structure of the natural intra- and intermolecular bonds in the starch polymer chains and the crystalline and amorphous fraction (Fig. 2, spectra 1a and 1b).

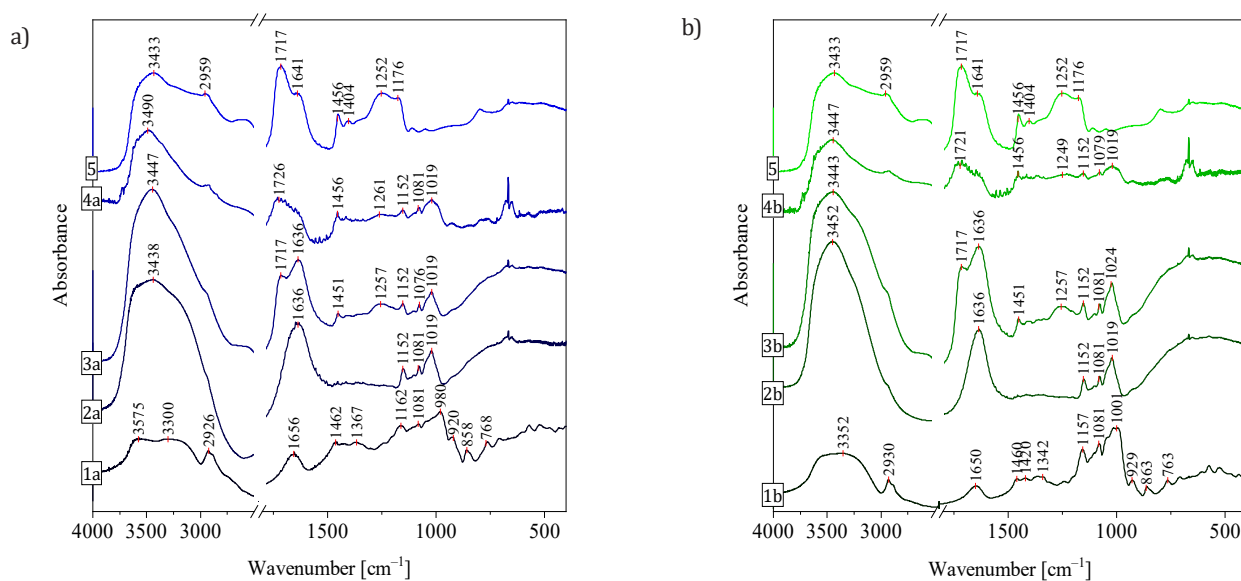


Fig. 2. Compilation of IR spectra: S_p (output) (1a), S_p (gelatinised) (2a), H-PA+ S_p (3a), H-PA+ S_p (dried) (4a), S_c (output) (1b), S_c (gelatinised) (2b), H-PA+ S_c (3b), H-PA+ S_c (dried) (4b) and PA solution (5)

The band maxima at 760 cm^{-1} , 851 cm^{-1} and 930 cm^{-1} confirm the presence of an α -1,4-glycosidic (C–O–C) bond typical for natural starch. Furthermore, on the IR spectra performed for samples 1, 2, 3 and 4, the existence of bands with maxima at wavenumbers 1015 cm^{-1} , 1094 cm^{-1} and 1163 cm^{-1} was observed, the formation of which also relates to vibrations characteristic of native starch (vibrations: C–O stretching, C–H bending, C–O and C–C stretching).

In the starch colloidal solutions S_p and S_c , the band in the range 3800–3000 cm^{-1} and the band at \sim 1636 cm^{-1} became more intense, which is related to the presence of solvent water (Fig. 2, spectra 2a and 2b). In the wave number range 3600–3000 cm^{-1} , the broad band corresponding to vibrations of the free O–H group (H_2O) and hydrogen bonds does not disappear after drying (spectra 4a and 4b). On the IR spectrum of the starting S_p sample in the region above 3000 cm^{-1} , two maxima related to the presence of intra- and intermolecular bonds were recorded: 3300 cm^{-1} and 3575 cm^{-1} . After drying, the course of the spectrum changes and shifts of the bands towards the wave number 3490 cm^{-1} are observed (spectrum 4a). This indicates changes in the hydrogen bonding region, including those occurring in the gelled starch-poly(acrylic acid) – solvent water relationship, and the presence of this band and the shifts in the maxima are probably due to the presence of hydrogen bonds in the hydrogel and the presence of bound water.

The structures of the considered fresh polyacrylate hydrogels H-PA1+ S_p and H-PA1+ S_c were almost identical (almost

without shifts), for example, the bands in the wavenumber range 1250–950 cm^{-1} and at wavenumber 1636 cm^{-1} did not change position compared to the S_p and S_c spectra, and these bands on the hydrogel spectra differed only in intensity (Fig. 2, spectra 3a and 3b). The broad band with a maximum at 1637 cm^{-1} on the colloidal solution spectrum was attributed to water adsorbed in the amorphous regions of the potato starch granule [22].

In dried/conditioned polyacrylate hydrogels involving native starch, no bands, other than those from either the acrylic polymer or the starch, were identified on the spectra, which may indicate that no chemical reaction with the formation of new groups took place between the components under hydrogel preparation conditions. Under conditions of air drying of polyacrylate hydrogels for 24 h, at 25°C and 30–45% humidity – a significant evaporation of solvent took place, as evidenced by changes in the shape and intensity of bands observed on spectra in the wave number range 3800–3000 cm^{-1} . In this range, a decrease in the height of a broad band was observed (Fig. 2, spectra 4a and 4b), but it is still relatively intense and its presence may indicate the existence of hydrogen bonds within the polymer chains – which allows the studied systems to be classified as physical hydrogels.

Table 2 contains data for the detailed identification of the characteristic absorption bands for the obtained IR spectra of the hydrogel H-PA+ S_p and H-PA+ S_c and their components.

Table 2
Characteristic absorption bands in the IR spectra of a sample of H-PA+ S_p and H-PA+ S_c hydrogel and its components

Spectrum									Vibration	References
1a/ S_p	2a/ S_p (colloidal solution)	3a/ H-PA+ S_p (hydrogel)	4a/ H-PA+SP (dried)	5/PA	1b/ S_c	2b/ S_c (colloidal solution)	3b/ H-PA+ S_c (hydrogel)	4b/ H-PA+ S_c (dried)		
Wavenumber [cm^{-1}]										
3300 –3575	3348	3447	3490	3433	3352	3452	3443	3447	O–H stretching /hydrogen bonding: O–H \cdots O–H; O–H \cdots O=H	[22–24]
2926	–	–	–	2959	2930	–	–	–	CH_2 deforming	[25]
–	–	1717	1726	1717	–	–	1717	1721	symmetrical stretching vibrations of the car- bonyl group (C=O)	[13]
1656	1636	1636	–	1641	1650	1636	1636	–	deforming H_2O	[23, 24]
1462	–	1451	1456	1456	1460	–	1451	1456	CH_2 bending symmetric deforming	[26]
1415	–	–	–	–	1420	–	–	–	CH_2 bending symmetric scissoring	[26]
1367	–	–	–	–	1342	–	–	–	C–H bending	[26]
–	–	1257	1261	1252	–	–	1257	1233	C–O stretching and	[13]
1162	1152	1152	1152	1176	1157	1152	1152	1152	C–O–H deforming	[22–24]
1081	1081	1076	1081	–	1081	1081	1081	1078	C–O, C–C stretching	[23]
980	1019	1019	1019	–	1001	1019	1024	1019	C–H bending	[22, 23]
920	–	–	–	–	929	–	–	–	C–O stretching, CH_2	[22, 23, 27, 28]
858	–	–	–	–	863	–	–	–	backbone vibration of α -1,4-glycosidic bond (C–O–C)	[23, 24]
768	–	–	–	–	763	–	–	–	C–H, CH_2 deforming	[23]

3.2. Determination of changes occurring in the hydrogel structure under increasing temperature conditions

Structural changes occurring in the obtained polyacrylate hydrogels with gelled native potato and cassava starches, in the presence of increasing temperature in the range of 25–200°C, were recorded online using the reflection technique of attenuated multiple reflectance spectroscopy (ATR-FTIR). The results are summarised as a series of IR spectra in the mid-infrared range 4000–600 cm^{-1} (temperature spectra, Fig. 3). Due to the large number of recorded spectra on the compilation, a discussion of the changes on the individual ATR spectra was omitted. The analysis was carried out by taking into account the disappearance or formation of bands, while isolating the temperature areas of the interpreted changes on the compilation of spectra.

The obtained results of structural studies of H-PA1+S_p and H-PA1+S_c hydrogels carried out under controlled heating conditions allow us to conclude that the prepared hydrogels show similar sensitivity to temperature change in the range 25–200°C.

In the temperature range from 25–200°C, bands presumably corresponding to vibrations of hydroxyl groups are observed on ATR spectra (area A, Figs. 3a and 3b) [29]. At 25°C, in the 3000–3800 cm^{-1} wavenumber range, a single band is present with a maximum at 3296 cm^{-1} for H-PA+S_p and 3350 cm^{-1} for H-PA+S_c. As the temperature increases to 125°C on the ATR spectra obtained, the bands in this region do not disappear, but their maxima shift towards lower wavenumbers. This indicates an intensification of the water evaporation process from the hydrogel sample. The process of releasing adsorbed water from the sample in the temperature range 120–150°C is also confirmed by the change in the shape of the band in the region of the wave number 1632 cm^{-1} (area B, Figs. 3a and 3b). At the same time, at temperature 125°C, a band associated with CH₂ deforming vibration appears from the slope of the band with a maximum at 2934 cm^{-1} originating from the poly(acrylic acid). In the temperature range up to 200°C, there were structural changes within the hydrogen bonds and evaporation of constitutional water, as evidenced by changes in the intensity and shift of band maxima in the range 3800–3000 cm^{-1} , but also by the formation of hydrogen bonding networks in the polymers of the dispersed phase of the hydrogel (poly(acrylic polymer), starch) (Figs. 3a and 3b, area A).

A gradual increase in temperature led to the appearance of bands or an increase in their intensity above 100°C in the wavenumber range 1500–1335 cm^{-1} (Figs. 3a and 3b, area C).

At the same time, these are not bands resulting from the formation of new chemical groups, but from the presence of groups characteristic of the poly(acrylic acid) from the polymeric system due to evaporation of the dispersion phase.

Changes in the 800–750 cm^{-1} range above 100°C indicate of structural changes within the starch monomers, and a shift in the maximum may indicate the onset of thermal degradation of the hydrogel (Figs. 3a and 3b, area D).

Table 3 presents an analysis of the characteristic absorption bands occurring in the areas highlighted in Figure 3 on the ATR-FTIR spectra of H-PA+S_p and H-PA+S_c hydrogels.

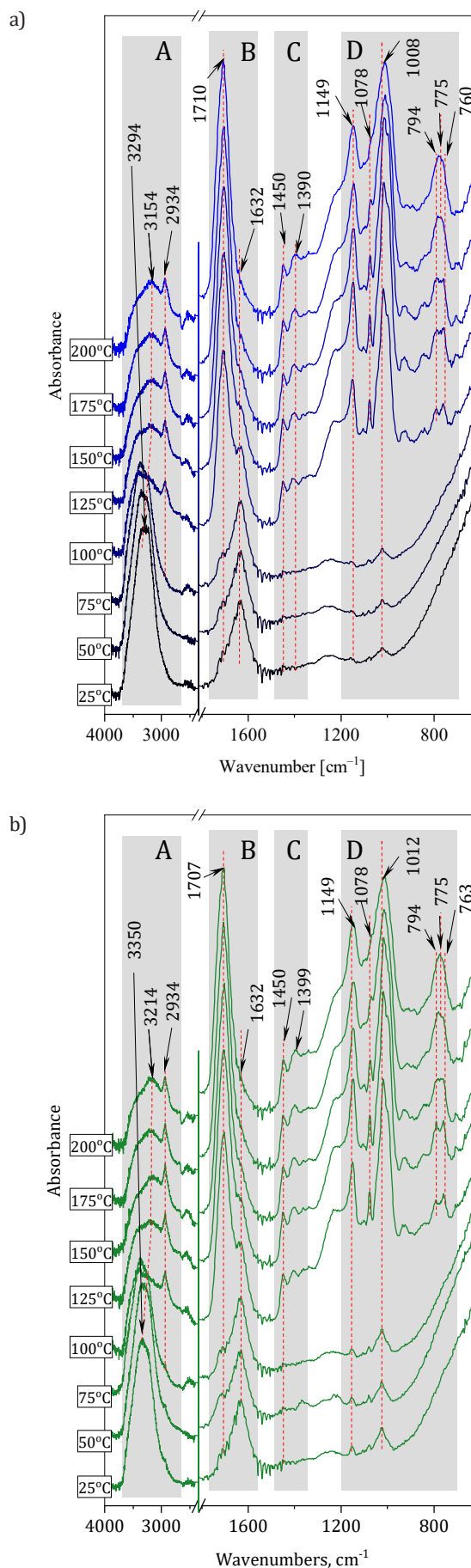


Fig. 3. A compilation of infrared spectra (ATR-FTIR) in the temperature range from 25–200°C: a) H-PA+S_p, b) H-PA+S_c

Table 3

Characteristic absorption bands in the IR spectra of polymeric hydrogel samples H-PA+S_p and H-PA+S_c and their assignment to the respective structure elements

Area	Wavenumber range [cm ⁻¹]	Temperature range [°C]	Vibration	Observed changes
A	3800–3000	25–200	hydrogen bonds: OH	decrease in intensity of the band with a maximum of 3294 cm ⁻¹ ; above 100°C shift of the maximum to 3154 cm ⁻¹ of the band
		100–200	C–H stretching	appearance of a band with a maximum at 2934 cm ⁻¹
B	1800–1545	25–200	deforming H ₂ O	fading of the band at 1632 cm ⁻¹
		100–200	C=O stretching	increase in intensity of the band with a maximum at 1710 cm ⁻¹
C	1500–1335	100–200	C–H symmetric bending	shift of the band maximum ~1390 cm ⁻¹
			CH ₂ symmetric bending deforming	band intensity change of 1450 cm ⁻¹
			(C–O)H	appearance of the band at 1149 cm ⁻¹
D	1200–600	100–200	C–H bending	disappearance of the band at 1078 cm ⁻¹
			C–O stretching, CH ₂	change in intensity and shape of the band at ~1010 cm ⁻¹
			C–O–C vibrations in the starch monomer ring	change in intensity and shape of the band with maxima at 794 cm ⁻¹ and ~760 cm ⁻¹ (disappearance of two maxima with formation of one at 775 cm ⁻¹)

4. CONCLUSIONS

On the basis of the research carried out and the analysis of the results obtained, the following conclusions can be drawn:

- the obtained results of structural studies conducted with the transmission technique (FTIR) confirm that, despite the different biological origin of natural potato and cassava starches, their chemical structure is very similar. The differences are manifested in the intensity of characteristic bands, e.g. those attributed to O–H vibrations (the presence of both intra- and intermolecular hydrogen bonds);
- the chemical structure of prepared polyacrylate hydrogels, irrespective of the biological source of the natural starch used, is almost identical; slight differences in the structure are manifested by the presence and intensity of characteristic bands, however, their location is the same in each case (within the measurement error limit);
- by comparing the IR spectra of fresh and dried hydrogel, a change in intensity and a shift in band maxima in the range of wavenumbers 3800–3000 cm⁻¹ was found, which testifies to the physical nature of the process of the transformation of liquid hydrogel to a solid form;
- thanks to the application of the ATR-FTIR technique, it was possible to assess differences in the sensitivity of hydrogels with both potato and cassava starch to an increase in temperature up to 200°C; in both cases, structural changes occurring under increasing temperature conditions followed a similar pattern, irrespective of the type of natural starch used; at a temperature of approximately 200°C, changes were noted that could be linked to thermal degradation of the bonds in the hydrogel.

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