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Hydrogels – a desirable alternative to water paper restoring procedures: impacting paper properties

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Water immersion is a common practice for treating paper media. However, this treatment could irreversibly damage paper and the information written on it – such procedures are advised if the documents do not contain water-resistant components such as inks or paints and the form is mechanically stable. Thus, polymeric materials are an attractive alternative to water immersion cleaning.

Various polymers are used to produce hydrogels, but there is not much information on cleaning effects before and after aging. Due to their highly rigid properties, Kelcogel, TopVision Agarose and Phytagel™ hydrogels could be applied to clean fragile paper media instead of water immersion. The hydrogel could safely clean without any residue or change of paper properties. Selected polymers were analysed for composition, water discharge and acidity according to the corresponding requirements for restoration processes: to establish changes in chemical and physical paper properties after hydrogel cleaning, filter paper samples were analysed with SEM, TGA, FTIR and pH-meter and compared to the benchmarks of filter paper cleaned with distilled water.

Keywords: hydrogels, paper properties, cellulose, cleaning

INTRODUCTION

Restoration and conservation of historical paper documents involve the removal of surface dirt and cellulose degradation by-products to reduce the acceleration of paper aging processes. Aqueous surface cleaning is by far the most used procedure. Cleaning by immersion improves the optical properties of historical paper and deacidification and reduces the presence of degradation by-products [1, 2].

The cleaning process is an essential step in paper restoration. However, the widespread cleaning procedure using a water setting may not be correct for all objects, as it could induce removal of sizing agents, paper fibres swelling, and dissolution or spreading of ink or paint components. Swelling cellulose fibres can cause sheet deformation, leading to mechanical strength loss. Moreover, immersion requires that water is replaced frequently during the procedure. To confront these issues, new materials – hydrophilic gels (hydrogels) – are being proposed as water medium substitutes. Hydrogels allow paper cleaning by dissolving water-soluble paper degradation products while reducing water uptake by paper [3–6].

Hydrogels are liquid-solid systems of solid water-based matrixes that can swell but do not dissolve in water forming a three-dimensional network. The network consists of hydrophilic polymers swollen in water or inorganic additives that increase viscosity and retention. The properties of the hydrophilic materials depend on the gelling agent, i.e. polymer functional groups (hydroxyl (–OH), carboxyl (–COOH), amide (–CONH–), sulfuric acid ($–SO_3H$) and others) [6, 7]. Also, these hydrogels could be used with other materials

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to improve their efficiency as paper restoration tools. Recently, hydrogels have been modified with various organic solvents, enzymes, neutralising agents, biocides, etc. to enhance and increase their capacity and selectivity in cleaning procedures. The hydrogel reduces the damage that water alone could inflict on paper objects by releasing water molecules onto the underlying historical paper. The hydrogel films absorb the dust and degradation compounds without any spread of ink or changes in ink colour [5, 8–10].

Nevertheless, improperly prepared hydrogels could leave a residue. Inefficiently removed hydrogel residue could induce microbial activity. To prevent these side effects, hydrogel must be a highly rigid film [10, 11].

Initial attempts to use hydrogels for paper-based cleaning began, at the ICPAL Institute (Instituto Centrale per il Restauro e la Conservación del Patrimonio Archivistico library) in Rome, Italy, in 2003 [10]. Due to its transparency, rigidity, hardness, the ability to isolate water while retaining the network structure of the polymer and absorb water-soluble products from degradation, the hydrogel has found more and more applications in the last four years, especially for a local stain remover, since prepared correctly it is non-stick and can be easily removed without damaging the surface of the paper [9, 12, 13].

This study aims to measure the change of acidity, thermo-resistance, polymerisation degree, and optical properties of paper samples affected by hydrogels Agarose, Kelcogel (low acylated Gellan gum) and Phytagel (deacytelated Gellan gum). The study assesses the change of thermo-resistance and optical properties of hydrogel and the quantity of water discharged by it.

EXPERIMENTAL

Materials

100% cellulose filter paper (ROTILABO® – round filters, type 111 A), surface weight 80 g/m^2, retention range 12–15 µm, filtration speed (according to DIN 53137) 10 s, pH of aqueous extract ~6.90, was selected for the study.

1. TopVision agarose (ThermoFisher SCIENTIFIC);
2. Gellan Gum Kelcogel CG-LA (GMW – Gabi Kleindorfer Shop, Germany);
3. Phytagel™ (Sigma-Aldrich Co. LLC);
4. $Cu(OH)_2$ (tech. 94% stab., Alfa Aesar GambH & Co KG, Germany);
5. Ethylenediamine (≥90%, Carl Roth GmbH + Co. KG, Germany);
6. Isopropanol (99.5% C_3H_7OH, Riedel-de Haën, Germany);
7. Ethanol (96% C_2H_5OH, Vilniaus degtinė, Vilnius).

Preparing hydrogels and cleaning samples

The research was performed on 125 (5 x × 5 cm) filter paper samples. Twenty four samples were cleaned in distilled water and hydrogels.

Standard samples were soaked in distilled water for 30 min, rinsed, distilled water was changed every 10 min, dried at room temperature and thermal-aged for 500 h in a drying oven at 85–88°C.

Hydrogels were prepared by adding powder (3 g for 3%) to distilled water (0.1 L). The resulting dispersions were heated by microwave oven at 700–900 W power for 1–2 min and then poured into ethanol-cleaned plastic containers to cool down. Obtained transparent films were laid on paper samples and kept for 1 h. After removing hydrogels, paper samples were dried at room temperature and thermal-aged for 500 h in a drying oven at 85–88°C.

To evaluate the effectiveness of the used materials and procedures, the treated paper samples and lyophilised hydrogels were characterised by different techniques and measurements, such as pH and water absorption, colour changes, infrared spectroscopy and scanning electron microscopy.

Evaluation of pH values

The pH value of the aqueous extract of filter paper sample fibres is approximately 6.90. Paper samples were cleaned with 3% unmodified hydrogels with pH values: 7.14 (3% TopVision Agarose), 4.74 (3% Gellan Gum Kelcogel CG-LA) and 5.41 (3% Phytagel™). For comparison, the filter paper was washed in distilled water at pH ~ 6.43.

A milled 0.1 g dry paper sample (weighed into 0.01 g accuracy) was filled with d 5 ml distilled water, which was boiled for 1 h for pH to reach 6.84 and then cooled down to room temperature. Prepared samples were left for 24 h to extract. Paper pH values were measured according to the cold-water extract pH measurement standard (ISO 6588-1; 2005) [14].

Extraction acidity was measured with a pH meter (Mettler Toledo MP220). One sample was measured with 0.2-unit accuracy, presenting an average pH value.

Thermogravimetric analysis

Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis was conducted to reference filter paper samples, and the filter paper samples were cleaned with 3% TopVision Agarose, Gellan Gum Kelcogel CG-LA and Phytagel™ hydrogels.

STA6000 Pyris 1 (Perkin-Elmer) thermal analyser was used for analysis (30–900°C, 10°C/min, nitrogen atmosphere).

Determination of the degree of cellulose polymerisation

The polymerisation degree was measured using a viscosimetric method of measuring fluid viscosity. Using a capillary viscometer (viscometer: type 53013; constant K 0.03; Cat. No. 9,268313) time of fluid flow from the reservoir through a narrow capillary was measured and polymerisation degree was determined according to international standards (ISO 5351/04) by dilute cupri-ethylenediamine solution by calculating dynamic viscosity [15].

The paper samples (100 mg) were dissolved in 25 ml 0.5 mol/l copper ethylenediamine (CED) and 25 ml distilled water with 1–2 mm pieces of copper wire solution. The viscometer was filled with 15 ml of the prepared solution. The experiment was conducted on a 25°C temperature thermostat.

Dynamic viscosity was calculated using Martin's formula

$$\eta_r = h \times t, \quad (1)$$

where η_r is dynamic viscosity, h is the calibration constant of viscometer K, s^{-1}, and t is time solution flows from the reservoir through the capillary, s.

After measuring the time of fluid flow, dynamic viscosity was calculated. The dynamic viscosity is related to the molecular mass. Mark–Houwink–Sakurada's empirical formula defines this relation:

$$[\eta] = K[M]^{\alpha}. \quad (2)$$

The connection between the dynamic viscosity and polymerisation degree (PD) in the celllose/CED system is expressed by the equation (Davis 1972)

$$[\eta] = K[PD]^{\alpha}, \quad (3)$$

where K is const. equal to –1.33 ml/g, [PD] is the cellulose/CED system degree, and a is the cellulose/CED system coefficient equal to –0.905.

The difference in polymerisation degree before and after thermal aging is convenient to express through the glycosylated bond number (δ, %):

$$\partial, \% = \left(\frac{1}{P} - \frac{1}{P_{Lo}} \right) \cdot 100. \quad (4)$$

SEM analysis of filter paper samples and hydrogels

The paper samples used for the research (4 × 4 cm) were observed with a Hitachi TM 3000 scanning electron microscope. After the lyophilisation (2–2.5 cm), hydrogels were analysed with a Hitachi SU70 average-resolution materials testing equipment.

Fourier transform infrared spectroscopy (FTIR)

Alpha FT-IR, Bruker was used to register FTIR spectra. The paper samples and pure materials spectra were captured between 4000–40 cm^{-1}. The spectra were analysed up to 2 r. u.

Colour change analysis of paper samples and hydrogels

The paper media and dried hydrogels were analysed with a FLAMES-VIS-NIR-ES spectrometer with a HL-2000-FHSA-20 W light source, resolution of ~1.5 nm, analysis time 2 s, measurement range 350–1000 nm. The used standard was the WS-1 Reflectance Standard (Fig. 1).

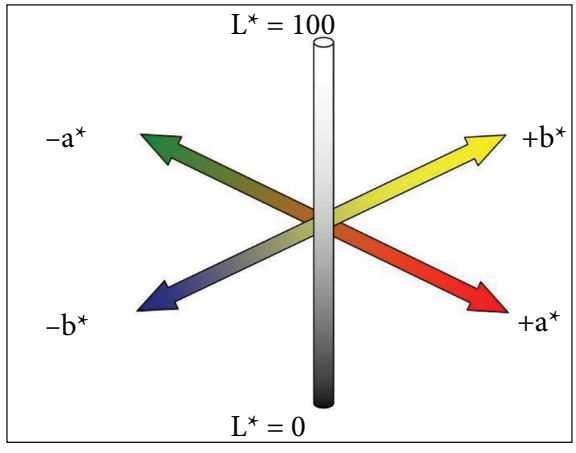

Fig. 1. CIELab coordinates [16]

There are three numerical values: L* for the lightness (from zero to hundred, black to white), a* and b* for the green-red and blue-yellow colour components. The colour change was calculated from the formula below [17]

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2), \quad (5)$$

where ΔL* is the difference in brightness, $\Delta L^* = \Delta L^*_S - \Delta L^*_0$ (S – standard, 0 – measured object), Δa* is the difference in red-green colour components $\Delta a^* = \Delta a^* - \Delta a^*_0$, and Δb* is the difference in yellow-blue colour components $\Delta b^* = \Delta b^*_S - \Delta b^*_0$.

Water discharged by hydrogel

Hydrogel's release of water and paper media water absorption were determined by a gravimetric method with CP 153-OCE scales. The samples were scaled before and after the cleaning procedure with 0.005 g precision. The absorbed water was calculated from the water absorption (WA) formula [18]

$$WA = \frac{M - M_0}{M_0}, \quad (6)$$

where M is the weight of the sample swollen in water, g, and M_0 is the weight of the sample dried at room temperature, g.

RESULTS AND DISCUSSION

The acidity of paper and hydrogel samples

Paper acidity is usually a consequence of cellulose degradation. Also, acidic compounds are sometimes embedded in the paper during production processes or in the presence of polluted air, ink and paint. The hydrogen ion rate (pH) helps evaluate the state of the paper and adopt the proper restoration procedures.

The received hydrogel pH values show that polysaccharides determine hydrogel acidity in their composition. The pH values of 3% TopVision agarose hydrogels are closest to neutral (pH ~ 7). The smallest pH values were shown by 3% Kelcogel CG-LA hydrogels, respectively 4.74. Phytagel™ hydrogels have weakly acidic properties: pH values of 5.41 for 3% hydrogels (Table 1).

According to the pH measurement standard (ISO 6588-1), two samples were compared to benchmarks:

Table 1. **pH values of hydrogel**

	Agarose	Kelcogel	Phytagel
Hydrogel (3%)	7.14	4.74	5.41

dried and pressed filter paper samples and thermally aged paper samples. Acidity measurements were also performed on filter paper after hydrogel cleaning samples. The results are shown in Table 2.

Table 2. **pH values of paper samples before and after cleaning treatments**

	pH values before thermal aging	pH values after thermal aging
Filter paper (FP) cleaned in distilled water	6.90	6.19
FP cleaned with 3% agarose hydrogel	7.15	6.84
FP cleaned with 3% Kelcogel hydrogel	6.34	6.08
FP cleaned with 3% Phytagel hydrogel	6.25	5.86

The most significant pH values after thermal aging were observed in the samples treated with 3% agarose, respectively 7.56, 7.10, 7.15 and 6.84. The lowest values were obtained in the samples washed with distilled water and treated with 3% Phytagel hydrogel.

Thermogravimetric analysis (TGA) results of paper samples and materials used for hydrogels

TGA allows examining the paper destruction degree. The TG graph indicates the chemical and physical changes of paper caused by hydrolysis, oxidation, or embedded components.

The results were compared to the benchmarks (distilled water-washed and unwashed samples) after and before 500 h of thermal aging. The analysis results are shown in Tables 3 and 4.

According to the temperatures at which most of the material is starting to decay (Fig. 3), TopVision agarose shows one phase splitting at 269°C temperature and a mass loss of 40%. Kelcogel and Phytagel have a similar expressed point of decay at 246 and 248°C temperatures, respectively. Both polysaccharides have a low acylation degree and a similar chemical composition. The mere difference between polysaccharides is the acyl group quantity.

Table 3. **Pure hydrogel mass loss and degradation temperature values**

Pure materials	Mass loss, %	The temperature degradation starts, °C
TopVision agarose	89	269
Kelcogel CG-LA	91	248
Phytagel™	92	246

Table 4. **TGA results of paper samples before and after thermal aging**

	Mass loss, %	Degradation temperature, °C	Mass loss, %	Degradation temperature, °C
		Before 500 h		After 500 h
Filter paper (FP)	97	353	98	347
FP washed in distilled water	98	350	98	344
FP cleaned with 3% agarose hydrogel	96	349	98	338
FP cleaned with 3% Kelcogel hydrogel	96	340	97	339
FP cleaned with 3% Phytagel hydrogel	98	339	96	337

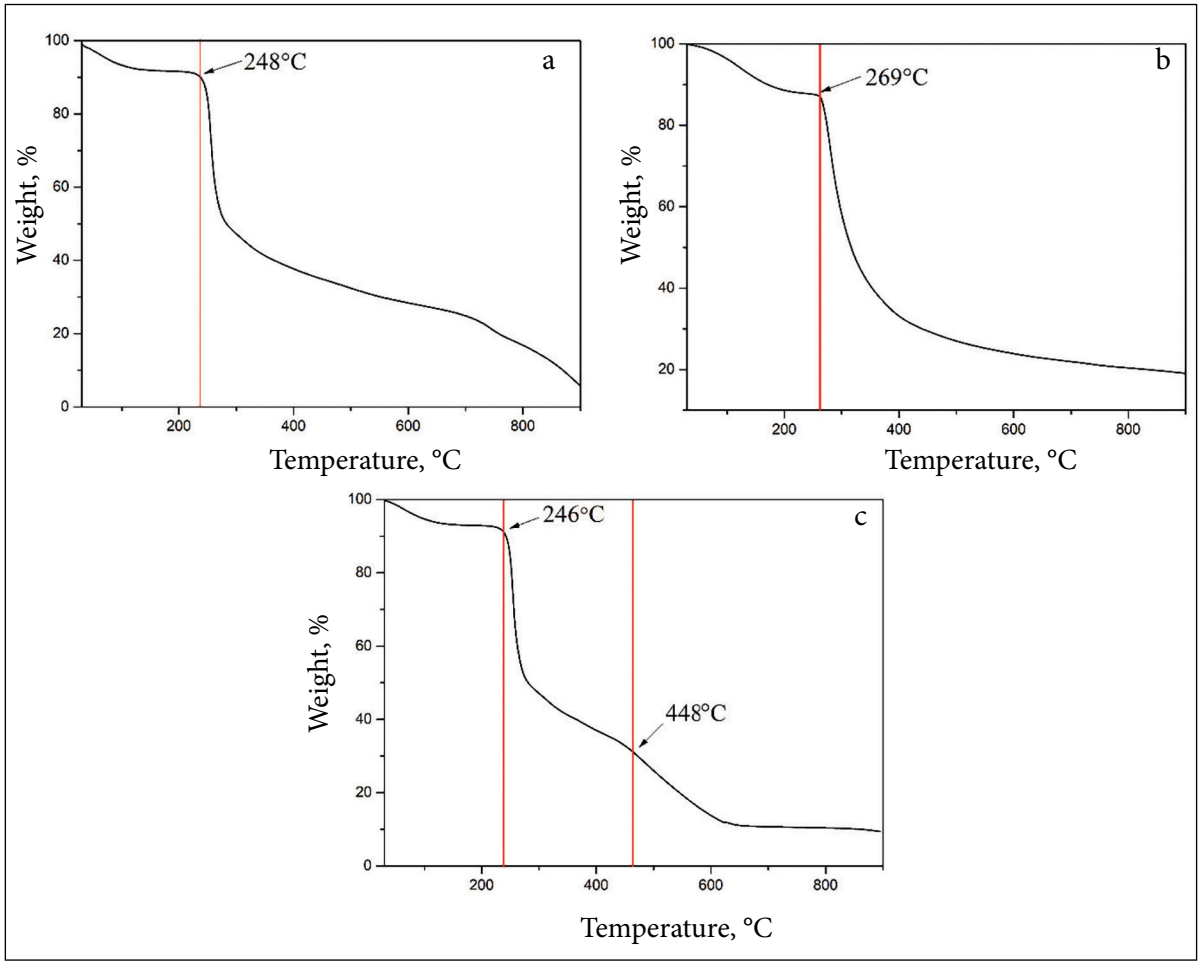

Fig. 2. Pure substances TG graphs: (a) TopVision agarose; (b) Kelcogel CG-LA; (c) Phytagel™ mass dependence from temperature

The lowest mass loss was shown in the filter paper samples treated with 3% agarose hydrogel and 3% Kelcogel hydrogel before thermal aging. The filter paper washed with 3% Phytagel had a mass loss similar to the samples treated with agarose and Kelcogel, respectively, 98, 96 and 96%.

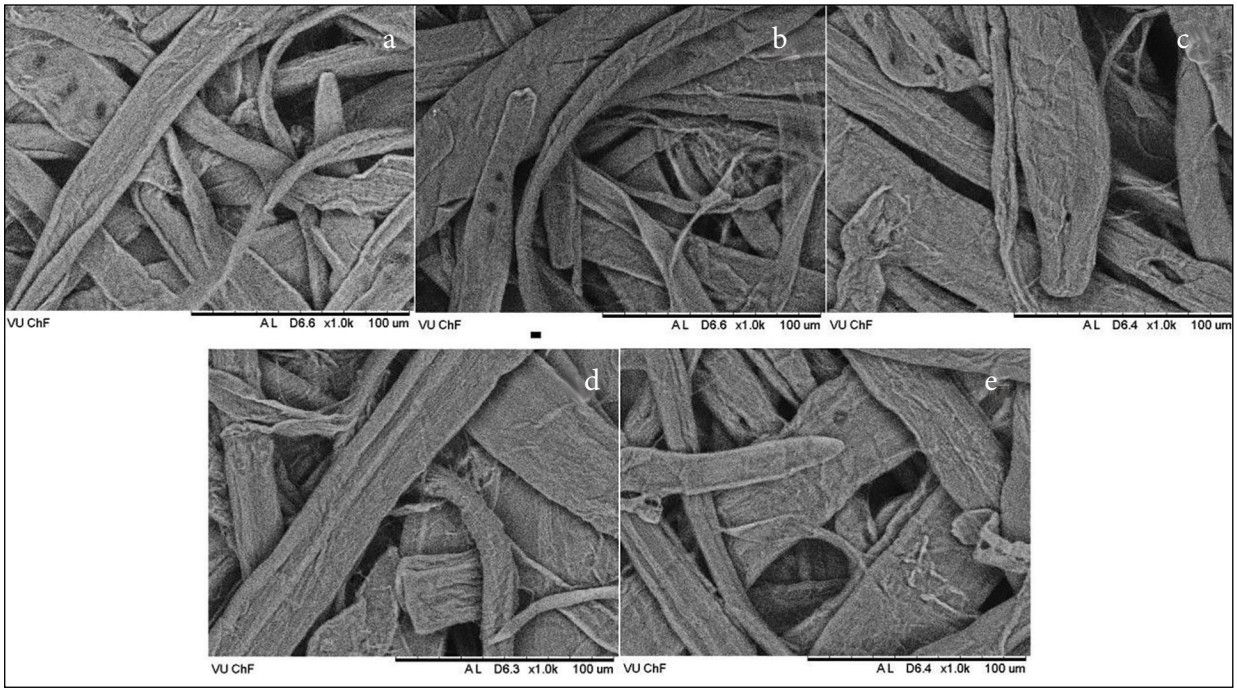

Fig. 3. SEM pictures of the paper samples cleaned with hydrogels and thermal aged for 500 h: (a) filter paper; (b) filter paper immersed in distilled water; (c) filter paper cleaned with 3% agarose hydrogel; (d) filter paper cleaned with 3% Kelcogel hydrogel; (e) filter paper cleaned with 3% Phytagel hydrogel

Nevertheless, after 500 h of thermal aging, the filter paper samples showed the opposite. Most of mass was lost in the paper samples treated with agarose hydrogel at 98%, the samples washed with Kelcogel lost 97% of their mass, and the lowest mass loss of 96% was preserved in the samples treated with 3% Phytagel.

Determination of the degree of cellulose polymerisation

Cellulose destruction is characterised by polymerisation degree (PD). The longer the cellulose chain, the more significant the molecular mass and polymerisation degree. Decreasing the polymerisation degree reduces mechanical strength and resistance. Lower PD indicates paper aging.

The shortening of the cellulose chain was preserved using the viscosimetric method of measuring fluid viscosity. After measuring the time of fluid flow, dynamic density was calculated. The results are shown in Table 5.

According to the results, the most considerable polymerisation degree before and after thermal aging is in filter paper samples 1053.9 and 1026.4 r. u. The paper samples washed by immersion show better results than the paper samples treated with hydrogel. The number of broken glycosylated bonds after washing the paper with distilled water is only 0.0007%.

The paper samples treated with hydrogels show a lower polymerisation degree of ~ 900 r. u. After thermal aging, the polymerisation degree of these samples decreased.

Table 5. **Polymerisation values of paper samples and amount of glycosidic bonds**

	Time cellulose/CED solution passes viscosimeter, s		Polymerisation degree, r.u.		Degraded glycosylic bonds, %
	Not aged	Aged 500 h	Not aged	Aged 500 h	Aged 500 h
FP	107.28	104.62	1053.9	1026.4	0.0021
FP + distilled water	104.44	103.61	1024.8	1015.9	0.0007
FP + 3% agarose	93.21	84.72	889.3	783.0	0.0153
FP + 3% Kelcogel	94.56	87.82	905.2	820.7	0.0114
FP + 3% Phytagel	92.95	90.48	885.3	853.7	0.0042

SEM analysis of filter paper samples and hydrogels

Hydrogels after lyophilisation and filter paper fibres were observed by scanning electron microscope to find out if washing procedures impact the paper structure. The paper samples treated with hydrogels and dried at room temperature were analysed. The SEM pictures are shown in Figs 4 and 5.

The SEM pictures show that the samples after washing procedures and thermal aging are not different from the reference samples. Fibres are not swelled. There are no fibre fractures or any other

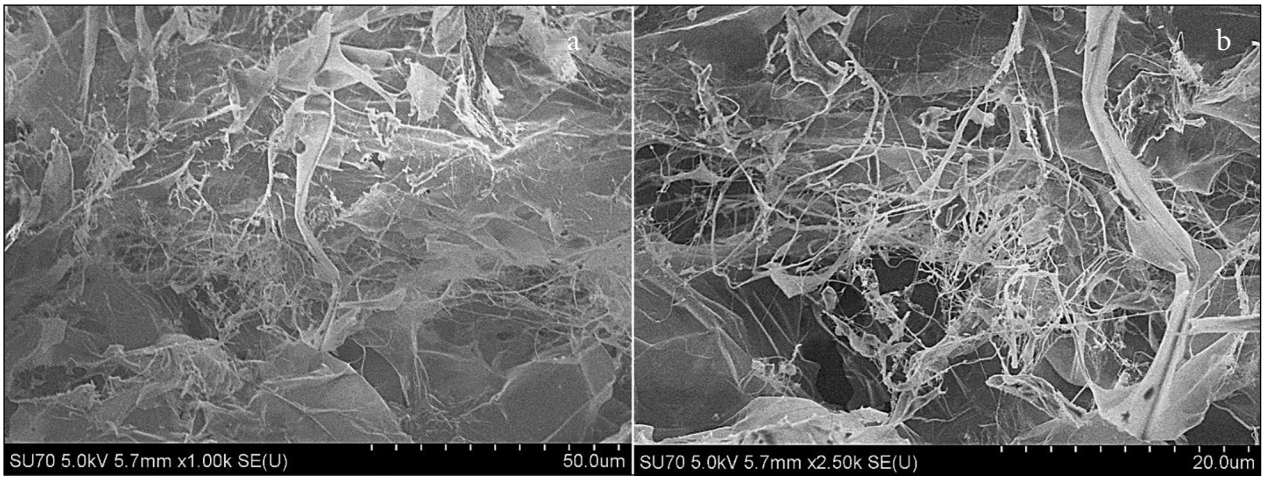

Fig. 4. Lyophilised 3% Kelcogel hydrogel SEM pictures: (a) before the cleaning procedure; (b) after paper media cleaning

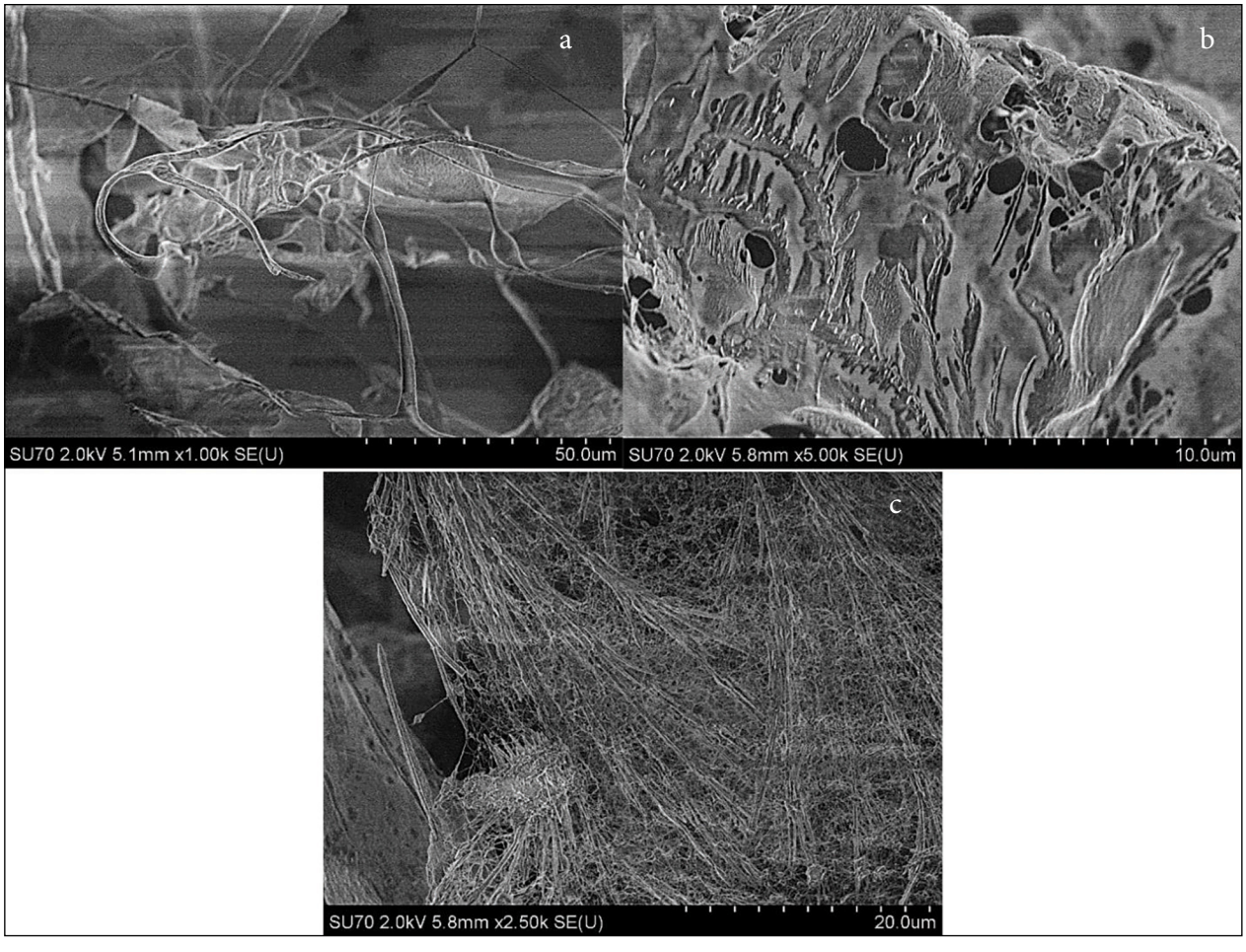

Fig. 5. Lyophilised hydrogels SEM pictures: (a) 3% agarose; (b) 3% Phytagel; (c) 3% Kelcogel

damage. During the process, there is no irreversible change in paper dimensions. The photos in Fig. 3 show that the Kelcogel hydrogel structure reminds a disordered net. The difference before and after thermal aging of the lyophilised hydrogel cannot be seen. Figure 6 shows the difference in the structure of Agarose, Kelcogel and Phytagel hydrogels. Agarose hydrogel (a picture) has a disordered large network structure.

On the contrary, Kelcogel and Phytagel form a smaller network structure. The Phytagel structure (Fig. 5a) reminds a honeycomb. The Kelcogel structure (Fig. 5c) has a network structure similar to a cobweb.

Fourier transform infrared spectroscopy (FTIR)

FTIR analysis was conducted to observe paper stability and aging processes during which functional groups of cellulose macromolecule change. Absorption bands define functional groups, while the intensity of bands shows their concentration. Throughout the analysis, polysaccharides and paper samples treated with hydrogels were analysed to determine what functional groups are present and how they affect paper aging processes (Figs 6–9).

Agarose is composed of the recurring dimer (1 → 3)-β-D-galactopyranose-(1 → 4)-3,6–anhydrous-α-L-galactopyranose. 1064 and 943 cm^{-1} peaks reveal C–O bond vibrations for 3,6–anhydrogalactose, 1064 cm^{-1} peak shows a glycoside bond, 1649 cm^{-1}, and broad 3367 cm^{-1} peaks identify OH groups of water absorbed in the surface. Also, persistent 2931 and 2843 cm^{-1} peaks of –CH– and $–CH_2–$ bond vibrations are observed in the FTIR spectra.

The structure of Kelcogel is a liner composed of recurrent glucose rhamnose and glucuronic acid chains. Large acyl group quantity polysaccharide has acyl substitutes instead of glucose molecule residue. Low acyl group polysaccharides could not contain any acyl groups. The FTIR spectra show an intensive peak at 1098 cm^{-1}, identifying as glycoside C–O bond vibration. The peak at 2930 cm^{-1} is –CH– group vibration, and the intensive peak at 1653 cm^{-1} shows the presence of the C=O acyl group. Also, a broad absorption band of the OH group is observed at 3343 cm^{-1} in the FTIR spectra.

Phytagel is an agar substitute synthesised from glucuronic acid, rhamnose and glucose. The FTIR spectra confirm the Phytagel composition. The intensive peak at 1084 cm^{-1} characterises C–O bond vibrations. 1650 cm^{-1} peak is specific to keto-aldehyde

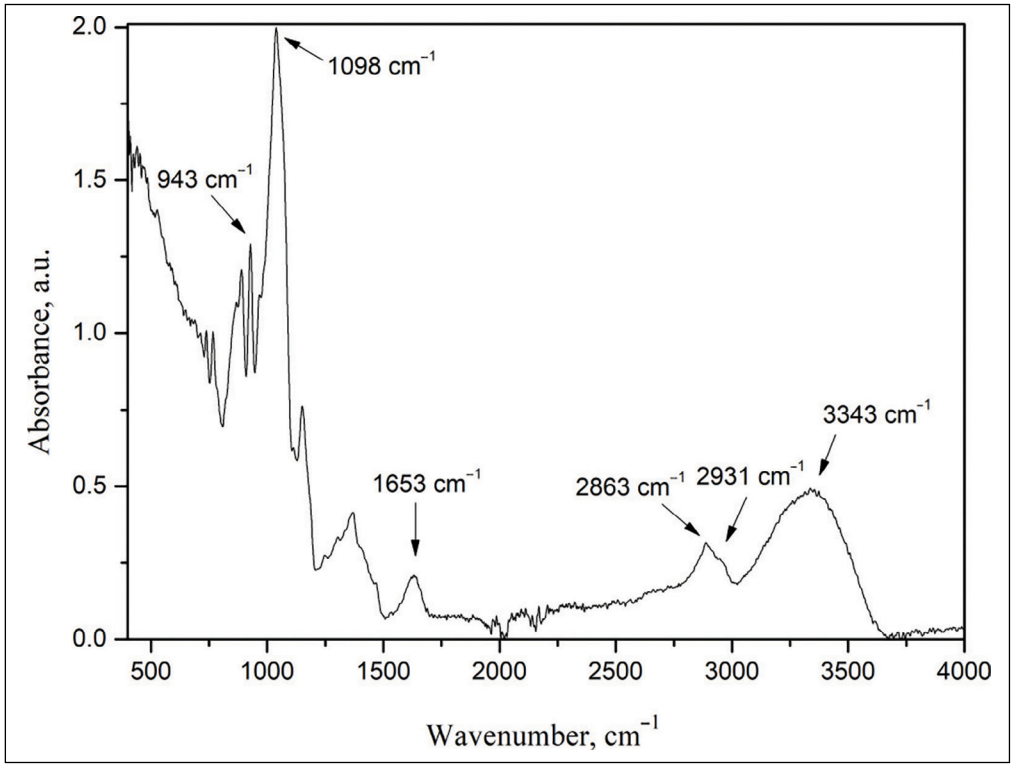

Fig. 6. TopVision agarose FTIR spectra

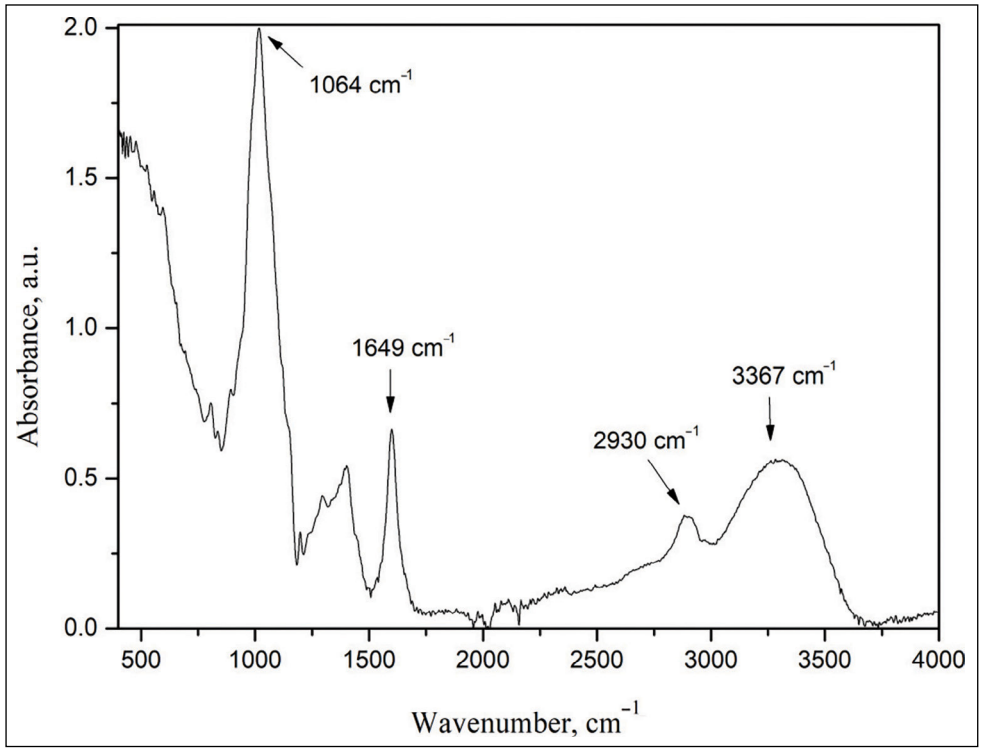

Fig. 7. FTIR spectra of Kelcogel

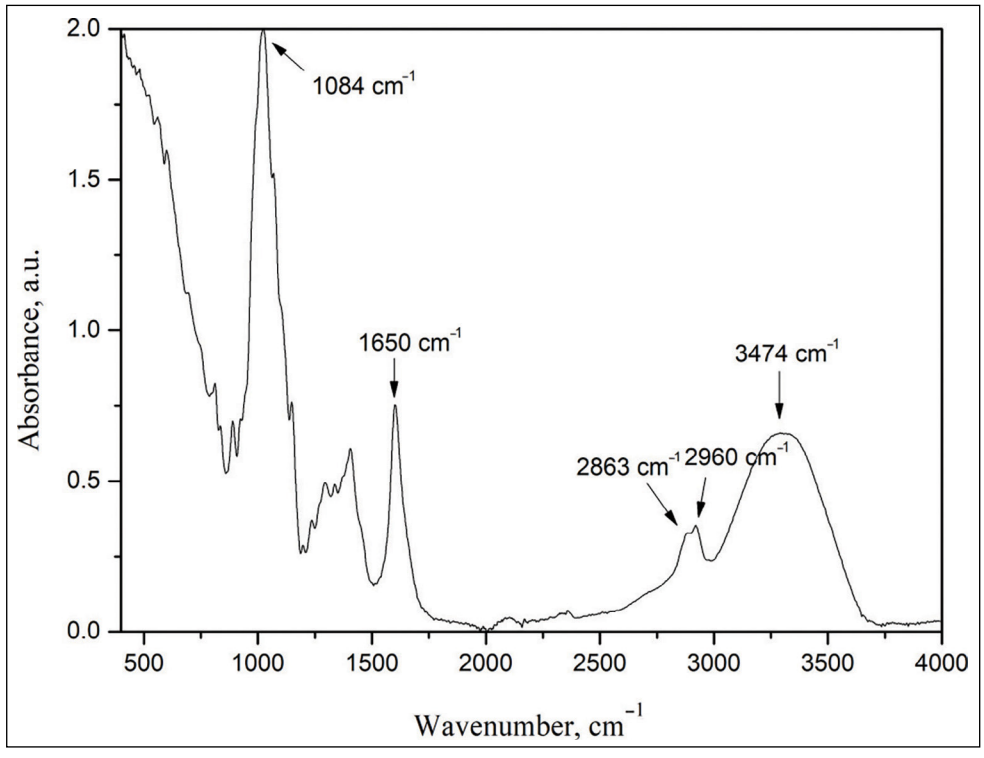

Fig. 8. Phytagel™ FTIR spectra

or carboxyl groups C=O bond vibrations. Similar to agarose, 2960 and 2863 cm^{-1} signals, respectively, identify –CH–and $–CH_2–$ groups vibrations, and 3474 cm^{-1} is the hydroxyl group signal.

All paper samples have shown a broad absorption band at 3250–3450 cm^{-1}, which stands for a hydroxyl group. Peaks at 2900–2800 cm^{-1} are vibrations at –CH– and $–CH_2–$functional group

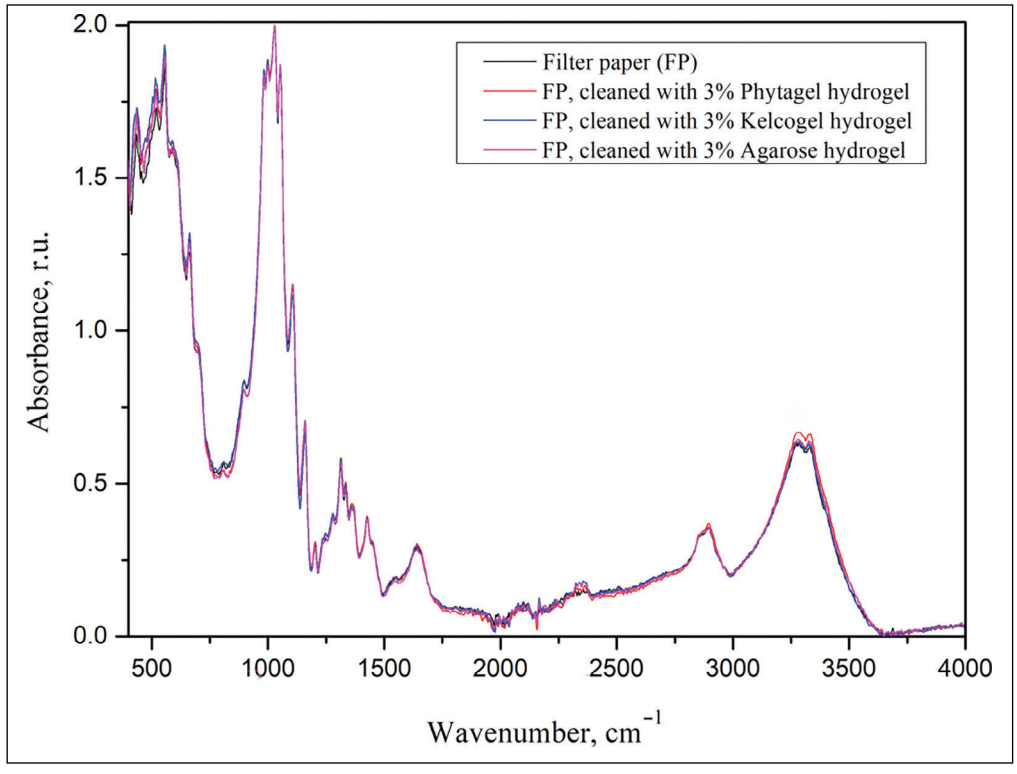

Fig. 9. Paper samples cleaned with 3% hydrogels and filter paper (benchmark FTIR spectra)

regions. Peaks at 1700–1617 cm^{-1} intervals show low-intensity keto, aldehyde and carboxyl groups. 1440 and 1250 cm^{-1} peaks identify as C–O bond vibrations. By comparison, the filter paper FTIR spectra are only slightly different from the FTIR spectra of paper samples treated with hydrogels. The intensity of peaks differs, while peaks from the filter paper and sample paper coincide. The same tendency is observed in the samples after accelerated aging.

Colour change analysis of paper samples and hydrogels

The main chromophores that determine discoloration are double –C=C– bonds along with keto groups (C=O). Colour change measurements were performed on the paper samples and hydrogel films before and after accelerated aging and cleaning procedures. Every sample was measured in a wavelength range of 350–1000 nm and located in CIELab coordinates (L*, a*, b*). The colour coordinates of the test samples and the estimated colour change are presented in Tables 6 and 7.

While comparing the results, it is easy to notice that the L* values for the filter paper standard and the paper cleaned with hydrogels do not differ much. It is safe to say that there are no radical changes in the object brightness after hydrogel cleaning.

Table 7 shows that the coordinates and colour change values in the paper samples aged 500 h are similar to ones where aging was not accelerated when the $\Delta E^* > 6$ change of discoloration is visible to the naked eye. After accelerated aging, the paper samples treated with Kelcogel and Phytagel hydrogels showed visible colour changes with ΔE^*, respectively, 9.843 and 9.826.

Water discharged by hydrogel

Water discharged by hydrogel depends on the concentration of polysaccharides. Choosing the wrong concentration of polysaccharides can do irreversible damage to paper media.

This research measured the amount of water released in 1 h from different concentration hydrogels (Fig. 9, Table 8). The results show that increasing the polysaccharide concentration in hydrogel decreases the amount of water discharged. 3% Kelcogel hydrogel releases 3.7% of its water, and 5% Phytagel releases 3.8% of its water in 1 h.

The research was also conducted on water amount changes while hydrogel was kept in the refrigerator

Table 6. **Paper samples colour coordinates and the estimated change value before thermal aging**

	CIELab coordinates			
	L*	a*	b*	ΔE* (sample/standard)
FP (standard)	82.045	0.120	–0.046	–
FP + 3% agarose hydrogel	80.987	0.283	0.331	1.139
FP + 3% Kelcogel hydrogel	80.718	0.335	0.087	1.353
FP + 3% Phytagel hydrogel	80.724	0.304	0.289	1.375

Table 7. **Paper samples colour coordinates and the estimated change value after thermal aging**

	CIELab coordinates after 500 h aging			
	L*	a*	b*	ΔE* (sample/standard)
FP (standard)	86.358	0.782	0.258	4.374
FP + 3% agarose hydrogel	83.231	0.56	3.096	5.043
FP + 3% Kelcogel hydrogel	90.456	0.558	3.006	9.843
FP + 3% Phytagel hydrogel	90.105	0.648	2.973	9.826

Table 8. **Water discharge**

	Weight, g		
	Initial	After one h	Dried
3% TopVision agarose hydrogel	22.286 g	19.826 g –11.5% (H_2O)	0.875 g
5% TopVision agarose hydrogel	18.983 g	17.734 g –7.1% (H_2O)	1.366 g
3% Kelcogel CG-LA hydrogel	10.783 g	10,403 g –3.7% (H_2O)	0.619 g
5% Kelcogel CG-LA hydrogel	29.684 g	29.236 g –1.6% (H_2O)	1.344 g
3% Phytagel™ hydrogel	23.209 g	22.330 g –3.9% (H_2O)	0.771 g
5% Phytagel™ hydrogel	14.856 g	14.333 g –3.8% (H_2O)	1.008 g

Table 9. **Kelcogel hydrogel refrigeration**

	3% Kelcogel hydrogel weight, g	
	In food film	In food box
Initial	19.700	17.877% (H_2O)
After 72 h refrigeration	19.530–0.9% (H_2O)	17.328–3.3% (H_2O)
After 192 h refrigeration	19.391–1.7% (H_2O)	15.272–14.1% (H_2O)
After 216 h refrigeration	19.360–1.8% (H_2O)	15.215–18.4% (H_2O)
After 360 h refrigeration	19.235–2.5% (H_2O)	13.059–39.1% (H_2O)
After 456 h refrigeration	19.073–3.4% (H_2O)	10.599–73.8% (H_2O)
Dried at room temperature	0.791	0.739

for 18 days. The results are presented in Table 8. After 19 days of holding 3% Kelcogel hydrogel refrigerated in a food container, the water loss was measured at ~74%. Nevertheless, 3% of Kelcogel hydrogels kept refrigerated in a food film lost only 3.4% of water. Agarose hydrogels have a tendency similar to Kelcogel hydrogels. According to the results, more prominent quantities of hydrogels can be prepared, stored in the refrigerator and used during the week.

CONCLUSIONS

The hydrogel cleaning method was tested on filter paper samples and characterised by different aging and paper properties. The results (before and after thermal aging) obtained from pH, TGA, polymerisation degree, SEM, FTIR, optical properties, and discharged water values were compared to the filter paper samples cleaned by immersion in distilled water. Introducing the tested hydrogels into the cleaning processes does not significantly impact the paper acidity or degree of polymerisation; it slightly changes the thermal stability of the paper. Examining the paper specimen with a scanning electron microscope revealed that fibre swelling and change of paper media dimensions are avoidable after hydrogel cleaning. No signs of destruction were observed even after 500 h of thermal aging. The colour change after accelerated aging can be seen in the paper samples treated with Kelcogel and Phytagel hydrogels $\Delta E^* > 0$. The investigated effectiveness of hydrogel cleaning showed that water immersion cleaning is still an irreplaceable method. Nevertheless, hydrogel cleaning is a better solution for the highly fragile paper medium, which cannot be soaked in water due to degradation or water-sensitive materials.

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HIDROGELIAI – ALTERNATYVA VANDENINĖMS RESTAURAVIMO PROCEDŪROMS: POPIERIAUS SĄVEIKA

Santrauka

Atsižvelgiant į popieriaus išsaugojimo svarbą, šio tyrimo tikslas – pritaikyti hidrogelius valymo procese bei ištirti jų poveikį popieriaus savybėms. Šio tyrimo metu buvo ištirtas popieriaus mėginių, paveiktų hidrogeliais („TopVision Agarose“, „Gellan Gum Kelcogel CG–LA“, „Phytagel™“), termoatsparumo, rūgščių ir optinių savybių kitimas. Tyrimui buvo pasirinktas filtravimo popierius, pagamintas iš 100 % celiuliozės. Popieriaus pavyzdžiai plauti hidrogeliais, džiovinti kambario temperatūroje ir termiškai sendinti iki 500 h džiovinimo krosnyje. Tyrimo metu buvo naudojami šie metodai: EDS/SEM, FT–IR spektroskopija, TG analizė, kolorimetrija, polimerizacijos laipsnis.