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New type of composite hydrogel based on natural polysaccharides and sodium polyacrylate for the production of fire-resistant fabrics

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Abstract Flexible and fire-resistant hydrogel–cotton fabric composites doped with ceramic fire retardants were obtained by the immersion method. Among the analyzed mixtures, the samples based on sodium polyacrylate, which provided the best degree of penetration and subsequent intumescence, and those containing magnesium hydroxide in their composition had the best fire-resistant parameters. This was confirmed based on TG/DSC and DMA thermal analysis, PCFC measurements, reaction to fire test results, and SEM microphotographs. The MIR spectroscopic analysis additionally proved that the fire-retardant mechanism is based on the creation of an intumescent structure strengthened by the interaction of fire retardants with various functions, such as hydroxides, which, during decomposition, create a protective char around the material. We believe that these results will contribute to the development of special fabrics with fire-retardant properties.

Keywords Fire-resistant fabric, Hydrogel composite, Intumescent system, Fire retardant, Vinyl polymers

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Introduction

Fire-retardant fabric is a type of a technical fabric that prevents the spread of fire or the impact of high temperatures after their source has been removed. It can be obtained in two ways. The first one is the use of special fibers with fire-retardant properties, such as polyaramid (obtained by polymerization of 1,3-diaminobenzene and isophthalic acid), polyamideimide (trade name Kermel), or polybenzimidazole fibers (known as PBI), which are woven in an appropriate way and are characterized by high decomposition temperature, great thermal and chemical stability, and also they are hard to ignite.[1–3] They are mainly used in commercial applications, such as clothing for firefighters and rally drivers, in the production of specialized rescue equipment, and in industrial fabrics (chair upholstery, carpets, etc.). Second way is to coat a standard fabric (for example, cotton, polyester, or polyamide) with substances that provide fire-retardant properties. Impregnations techniques are soaking, layer-by-layer method, direct polymerization, sol–gel precipitation or even sewing laminates, and a fabric.[4–14]

Untreated natural cotton is one of the most flammable textiles with an LOI (limiting oxygen index) of only 18.4%. Its decomposition starts at about 300°C and reaches maximum at about 364°C in air (375°C in nitrogen). Initially, fire retardancy of cotton consisted of chemical treatment using mainly phosphate flame retardants (for example, ammonium polyphosphates (APP) and N-methylol dimethylphosphonopropionamide (MDPA)). They are still used, but currently they are multicomponent systems, such as systems with PDMS (polydimethylsiloxane) and carboxylate derivatives. Hydrogel systems, which additionally provide, for example, better elasticity of the fabric, are also used.[15–17]

In the case of hydrogel systems, they are used as covering layers or internal fillings between the layers of composite material. To ensure the adequate fire-retardant parameters of the composite, where the hydrogels themselves constitute a thermal barrier during contact with fire, their combinations are most often used. For example, Yu et al., using soaking method, applied a layer of hydrogel on cotton fabric consisting of a combination of poly(N-isopropylacrylamide)/sodium alginate/poly(vinyl alcohol) (PNIPAAm/SA/PVA). As a result of this treatment, the thermal parameters of the composite improved significantly. LOI increased from 18% for pure fabric to even 29% in the case of the composite, for which no afterglow was also observed.[6] They have also tested the poly(N-isopropylacrylamide) and sodium alginate (PNIPAAm/SA) system, also achieving improved fire-retardant properties.[9,10] In turn, Pan et al., using the layer-by-layer method, used a combination of phosphorylated poly(vinyl alcohol) with chitosan (PPVA/CS), where the phosphate group in PVA can be considered as an additional fire retardant. By increasing the number of layers from 10 to 30, the following results were obtained: reduction in the Heat Release Rate peak (pkHRR) and the reduction of the amount of gases released during the fire test. What's worth noting here, is that a large number of layers were required.[12] A similar solution was used by Wang et al. They obtained systems in which bilayers of nitrogen-modified silane and phytic acid (SiN/PA) were applied to the cotton fabric.[14] Other solutions in this area include the use of the carboxymethyl chitosan/aminated carbon nanotubes (CCS/ACNTs)[18] or ammonium alginate/phytic acid@trimethoxy(octyl)silane (AA/PA@TMOS) systems. Also here, the fire-retardant effect is enhanced by the use of the functional groups, i.e., ammonium derivatives.[19]

The disadvantage of the above-mentioned solutions, despite the obvious improvement of the thermal properties, is the time-consuming process, often requiring the application of many layers and the associated stages of drying, gelling, etc. The solution here may be the introduction of the fire retardants directly into the hydrogel structure as a result of mixing, and not through the chemical modification of the polymer chain, what further simplifies the process of preparing the impregnating mixture. This publication attempts to answer the above-mentioned problem. The influence of the three-component fire-retardant systems (from magnesium hydroxide, aluminum hydroxide, zirconium oxide, mineral fibers, and glass fibers) and the type of the used hydrogel (chitosan, sodium alginate, and sodium polyacrylate) on the fire-retardant properties of the pure and pretreated cotton fabrics impregnated with them, were tested. Based on the results of TG/DSC thermal analysis, MIR spectroscopy, SEM analysis, and fire tests, the mechanism of formation of the fire-retardant layer and the influence of individual components on the fire-retardant properties of the developed composites were determined. In the next part of the research, this information will allow us to design the fire-retardant hydrogel for use as the protective layer for fabrics used as the curtains or upholstery, but mostly as the element of the composite materials used in technical fabrics. We will answer the question whether the number of required layers can be reduced by using a higher content of the mentioned retardants. It will also contribute to the development of the knowledge in the field of the fire-retardant materials.

Materials and methods

Materials

Raw cotton fabric (CF) with a grammage of 145 g/m^2 was selected as the material laminated with hydrogel. The

Table 1: List of the used materials

Description	Abbreviation	Source
Cotton fabric	CF	Katel, Poland
Sodium hydroxide	NaOH	Avantor Performance Materials, Poland
Acrylic acid	AA	Acros Organics, Belgium
Potassium persulfate	KPS	Avantor Performance Materials, Poland
Sodium thiosulfate	NTS	Avantor Performance Materials, Poland
N,N´-methylenebisacrylamide	NNMBA	Acros Organics, Belgium
Chitosan	CH	Fisher Scientific, USA
Sodium alginate	SA	Biomus, Poland
Acetic acid	Ac	Avantor Performance Materials, Poland
Calcium chloride	$CaCl_2$	Biomus, Poland
Aluminum hydroxide	$Al(OH)_3$	Chempur, Poland
Magnesium hydroxide	$Mg(OH)_2$	Chempur, Poland
Zirconium oxide	ZrO_2	Avantor Performance Materials, Poland
Glass fibers	GF	Schwarzwalder Textil-Werke, Germany
Mineral fibers	MF	Schwarzwalder Textil-Werke, Germany

material was pretreated using an 18 wt% aqueous sodium hydroxide (NaOH) solution synthesized in the laboratory. The following polymers were used as the hydrogel substrates for lamination mixtures: sodium polyacrylate (ANa; also synthesized in the laboratory, according to the procedure described elsewhere[20]), sodium alginate (SA), and chitosan (CH). Substances mentioned below were used as the fire retardants which were introduced into the hydrogel network: magnesium hydroxide ($Mg(OH)_2$), aluminum hydroxide ($Al(OH)_3$), zirconium oxide (ZrO_2), glass fibers (GF) of medium length of 150 µm, and mineral fibers (MF) of medium length of 20 µm. All of the used substrates, modifying factors and initiators are listed in Table 1. All reagents were used without further purification.

Pretreatment procedure of the cotton fabric

In order to analyze the characteristics of each lamination mixture, we have prepared cotton fabrics that have been pretreated to make it easier for the mixture to penetrate deeper by widening the cellulose pores.[21,22] Pretreatment was performed by immersing pure cotton patches in an 18 wt% aqueous sodium hydroxide solution for 5 min. After that, the fabrics were rinsed with distilled water to neutral pH and dried in room temperature atmosphere (Fig. 1). To check the correctness of the procedure, SEM microphotographs were taken. Microgrooving patterns and uneven surface were observed on the pretreated cotton fibers (Fig. 2), what indicates the opening of the fibers.

Preparation of the hydrogel lamination mixtures

First, solutions of the pure hydrogels were prepared. In the case of sodium acrylate, it was 20 wt% aqueous monomer solution, while in the case of sodium alginate, it was 1.5 wt% aqueous solution. A 1.5% chitosan solution was prepared by dissolving it in a 3 wt % aqueous acetic acid solution. In the next step, fire-retardant powders were gradually introduced into the hydrogel solutions to obtain three-component mixtures

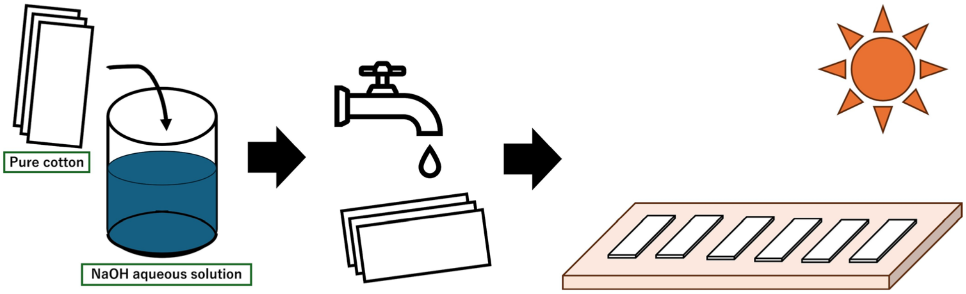

Fig. 1: Draft of the pretreatment of the cotton fabric

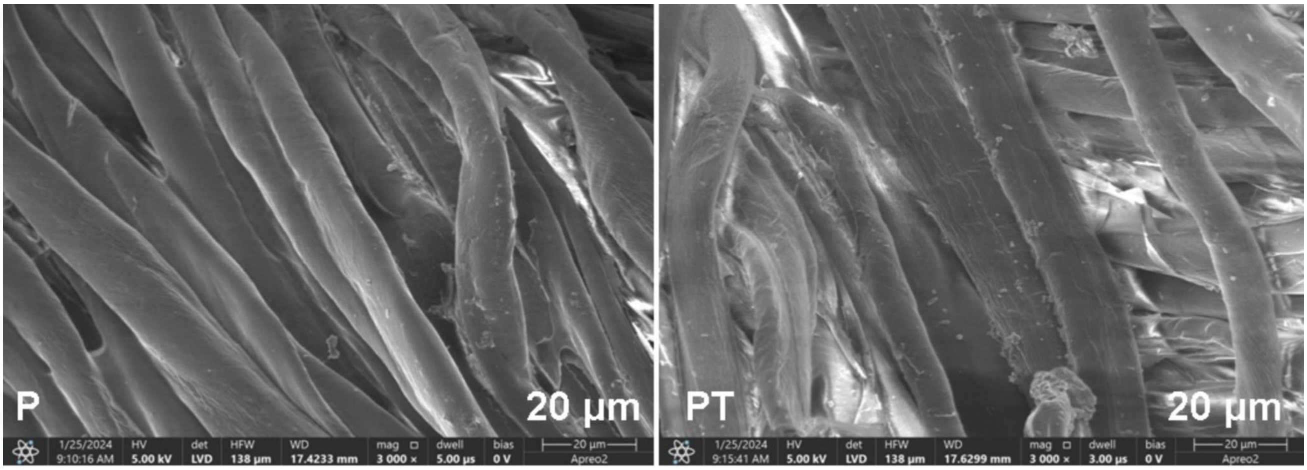

Fig. 2: SEM microphotographs of the pure (P) and pretreated (PT) cotton fabrics

with 2 wt% of each retardant. Table 2 contains the exact compositions of the described mixtures.

Impregnation process

In order to examine the fire resistance of each hydrogel mixture, they were applied to the two types of cotton fabrics, i.e., pure and pretreated. Samples with sodium alginate mixtures were leaved in the freezer for 24 h. After taking out, they were completely thawed, immersed in 3 wt% $CaCl_2$ aqueous solution to obtain a gelled laminate, and dried at room temperature (Fig. 3). In the case of samples with chitosan mixtures, after application, they were leaved for 24 h in the containers, then drained and dried at room temperature atmosphere to be laminated. Applying sodium acrylate to cotton fabrics, 0.3 wt% of the cross-linking monomer (NNMBA) and the same amount of the redox initiators (KPS/NTS) were added to each mixture before application. Then, cotton fabrics were immersed in such prepared mixtures for 30 min, drained and dried at room temperature. Obtained samples were marked as follows:

number of the mixture/type of the used hydrogel/type of the cotton fabric,

where:

- number of the mixture—symbol of the composition from Table 2 (from 1 to 8),
- type of the used hydrogel—sodium alginate (SA), sodium polyacrylate (ANa), or chitosan (CH),
- type of the cotton fabric—pure (P) or pretreated (PT).

In the case of sodium alginate and sodium polyacrylate, samples containing all the compositions from Table 2 were prepared, while in the case of chitosan, samples with compositions not containing magnesium hydroxide, i.e., only 3–6, were prepared, because Mg $(OH)_2$ caused gelation of this polymer solution.

Table 2: Composition of the three-component hydrogel mixtures

Symbol of the composition	Component I [2 wt%]	Component II [2 wt%]	Component III [2 wt%]
1	$Mg(OH)_2$	ZrO_2	GF
2	$Mg(OH)_2$	ZrO_2	MF
3	$Al(OH)_3$	ZrO_2	GF
4	$Al(OH)_3$	ZrO_2	MF
5	ZrO_2	GF	MF
6	$Al(OH)_3$	GF	MF
7	$Mg(OH)_2$	GF	MF
8	$Mg(OH)_2$	ZrO_2	$Al(OH)_3$

Characterization methods

Thermogravimetry/differential scanning calorimetry (TG/DSC) measurements were made to examine the influence of the impregnation mixture on the thermal properties of the composite samples, i.e., degradation and stability. The measurements were conducted by using a STA 449 F3 Jupiter (NETZSCH) thermal analyzer and aluminum oxide crucibles in nitrogen protective atmosphere. The tested cellulose samples were kept at 21°C for 2 min to stabilize their temperature and then heated up from 21 to 700°C at 2°C/min step.

Flammability of the fire-resistant cotton fabrics was evaluated using a Pyrolysis Combustion Flow Calorimeter (PCFC) from Fire Testing Technology (FTT). Small amount of sample (5±1 mg) was heated up in pyrolysis chamber to 750°C in nitrogen atmo-

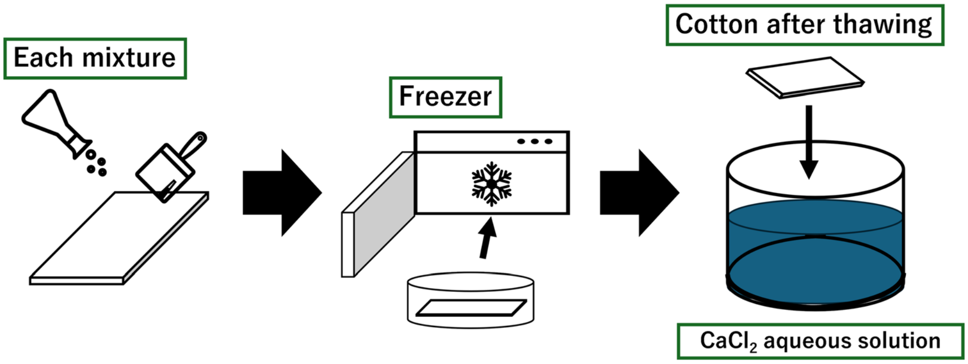

Fig. 3: Draft of the impregnation process involving sodium alginate mixtures

Table 3: Results of the reaction to fire

Symbol of the sample			Smoke*	Extinguishing the fire**	Unburnt area [%]***
Control sample (pure cotton)			M	W	5
1	SA	P	S	A(3s)	90
		PT	S	A(8s)	80
	ANa	P	S	A(1s)	80
		PT	S	–	95
2	SA	P	S	W	85
		PT	S	A(5s)	80
	ANa	P	S	A(3)	85
		PT	M	W	80
3	SA	P	M	W	50
		PT	S	–	70
	ANa	P	S	A(4s)	95
		PT	S	–	90
	CH	P	S	A(7s)	70
		PT	S	A(6s)	60
4	SA	P	S	A(5s)	85
		PT	S	A(6s)	85
	ANa	P	S	A(7s)	85
		PT	S	W	60
	CH	P	S	A(4s)	85
		PT	–	–	85
5	SA	P	S	A(6s)	60
		PT	S	A(6s)	40
	ANa	P	S	A(8s)	85
		PT	M	A(8s)	60
	CH	P	S	W	70
		PT	S	A(9s)	50
6	SA	P	S	–	90
		PT	S	A(10s)	60
	ANa	P	M	A(11s)	85
		PT	S	A(3s)	95
	CH	P	S	–	90
		PT	–	–	80
7	SA	P	S	A(11s)	80
		PT	S	W	30
	ANa	P	S	A(6s)	80
		PT	–	–	98
8	SA	P	S	A(10s)	90
		PT	S	–	90
	ANa	P	S	–	97
		PT	S	A(4s)	85

*Smoke: S→Small amounts of white smoke, M→Medium amounts of white smoke, –→No smoke

**Extinguishing the fire: W→extinguishing with water, A(…s) self-extinguishing after … seconds, –→no flame on the sample after removing the burner

***Unburnt area [%]: ratio of the unburned surface after the fire test to the surface of the sample before the fire test [%]

sphere with a heating rate of 1°C/s. After that, the gases produced by pyrolysis were oxidized in a high-temperature furnace at 900°C. Pyrolysis was carried out at a controlled O_2/N_2 atmosphere with a flow rate of 20/80 cm^3/min. Based on the obtained results, we have calculated the following parameters: heat release capacity (sumHRC) [J/g K], heat release rate (HRR) [K/s], total heat release (THR) [kJ/g], and residue [wt %].

Dynamic mechanical analysis (DMA) was used to study the effect of temperature treatment on the mechanical properties of the cotton samples. To evaluate the viscoelastic behavior of the composites, we have measured samples in tension mode with a Netzsch DMA 242 E Artemis analyzer. Samples with average dimension of 10 mm × 6.5 mm × 0.45 mm were used. Experiments were carried out in the temperature range from −50°C to 200°C with a heating rate of 3°C/min. Variable frequencies of 1 Hz, 5 Hz, 10 Hz, and 20 Hz were used. This test was performed twice, on the same samples and under the same measurement conditions. To assess the temperature influence on the stability of the hydrogel coating, we have tested samples in the shear sandwich mode using the same analyzer, temperature range, and frequencies. The only difference were in the shape (round) and the dimension of the samples (average diameter of 10 mm and average thickness of 0.6 mm).

Further verification of the effect of the tested impregnation mixtures on cotton flammability was done using the test called the reaction to fire. Samples of 10 cm long and 1 cm wide were exposed to a Bunsen burner flame for 15 s in a horizontal arrangement, with the shorter side directly touching the flame during the test. Flame propagation, degree of combustion, and the amount of emitted smoke were assessed. The size of the burned/unburned area was estimated using the computer-aided planimetric method.

Thermo Fisher Scientific Apreo 2SEM scanning electron microscope equipped with a ChemiSEM EDS analyzer was used for observation of the samples surface before and after the fire test. Before the analysis, samples were carbon-coated using an Leica EM ACE600 sputter coater and then observed in high vacuum mode.

The aim of the IR analysis was to determine the functional groups of substances remaining in the samples after the fire tests. Bruker Vertex 70v FTIR spectrometer was used for this purpose. Samples in the form of KBr pellets were tested. The spectra were recorded in the range of 400–4000 cm^{-1}, averaging 25 scans and using a resolution of 1 cm^{-1}.

Results and discussion

Reaction to fire

Table 3 contains the results of the reaction to fire test, whereas Fig. 4 shows pictures of the selected samples after this test.

Grayish pumice appeared on the burned parts of the impregnated samples in most cases, what indicates that these samples show some fire-resistant effect compared to the pure cotton after the fire test. As a result of observations made during the test, it was noticed that each of the tested groups of the impregnated fabrics showed characteristic behavior. For example, when comparing samples of impregnated pure cotton fabrics and pretreated fabrics, it was found that in most cases, the pretreated samples had better properties, as they self-extinguished faster than their counterparts on pure fabric, emitted less smoke, and burned to a lesser extent. This proves deeper impregnation and a stronger cellulose fiber-hydrogel bond. Comparing the type of hydrogel, the best properties were demonstrated by the samples impregnated with sodium polyacrylate. They burned/charred the least and spontaneously extinguished faster after removing the flame. Next came the chitosan-based samples, and finally the sodium alginate samples. When analyzing compositions of the retardants and the degree of sample combustion, the best properties were demonstrated by the mixtures 1, 7, and 8, each of which contained magnesium hydroxide. During the thermal decomposition, hydroxides decompose into the oxides and water vapor, and the oxides activate the formation of a stronger protective char around the material.[23–25]

TG/DSC analysis

Analyzing the TG/DSC thermograms, no major differences were found between samples with chitosan and sodium alginate, while in the case of samples with sodium polyacrylate, differences were visible, for example, in an additional peak on the DSC curve at temperatures above 510°C (Fig. 5) or a smaller mass loss on the TG curve (Fig. 6). There were also no major differences between the used cotton fabrics, i.e., pure or pretreated. Up to a temperature of 350°C, the loss in the TG curves of samples with sodium polyacrylate was about 40 wt% and above–30 wt%. For samples with chitosan and sodium alginate, these values were 50 wt% and 30 wt%, respectively. These differences could be related to the initial viscosity of the hydrogel mixtures, which were approximately 100 mPa s for mixtures with sodium polyacrylate and 200–380 mPa s for mixtures with chitosan and sodium alginate. Fluids with lower viscosity penetrated the cotton fabric more easily, adhering to the fibers of the material more thoroughly, thus providing better protection. This is confirmed by the SEM microphotographs (Fig. 8). Additionally, for samples with sodium polyacrylate, the weight loss was three-stage, while for samples with chitosan and sodium alginate, it was a two-stage process.

Exothermic peaks in the DSC curves occurred in four temperature ranges, i.e., 310–350°C, 390–420°C, 440–500°C, and just above 510°C (Fig. 5). They were characterized by different intensities, with peaks above 440°C related to the biggest exothermic effect. Additionally, a small endothermic peak at a temperature of approximately 50–80°C, related to the loss of water and moisture contained in the tested samples, was noticeable on all of the curves. Peaks in the range of 310–350°C were associated with the beginning of decomposition of the cotton fabric and polymers contained in the tested composite samples (for example, monomer dehydration and decomposition of polymer bonds). It can be also concluded that the addition of the fire retardants and related to them transformations shifted these values toward higher temperatures, because according to the literature data, this effect starts at a

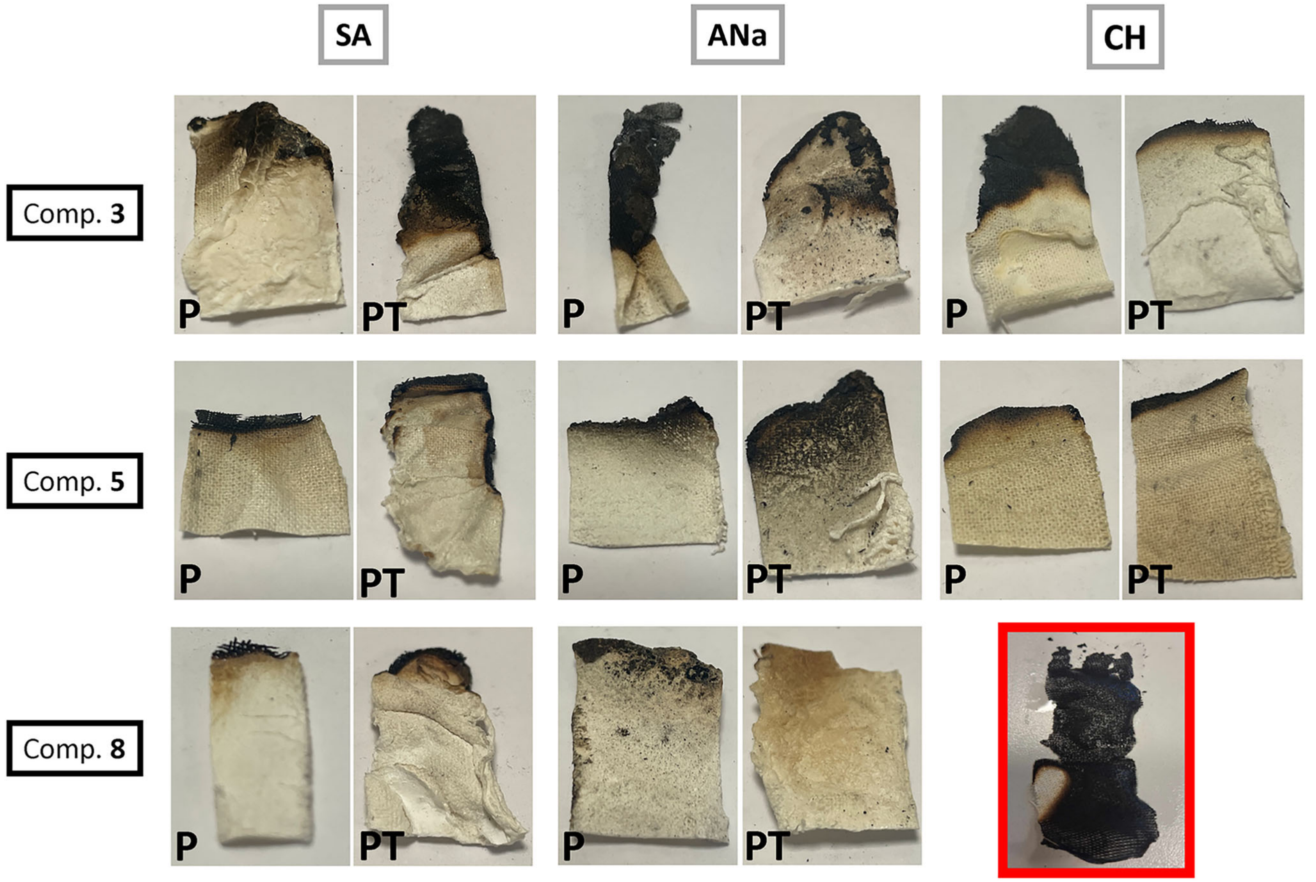

Fig. 4: Surface of the selected impregnated samples after the fire test compared to pure cotton (red frame)

temperature of about 300°C for pure cellulose and sodium polyacrylate and 250°C for sodium alginate and chitosan. Peaks in the temperature range of 390–420°C were only visible for samples with sodium polyacrylate and chitosan and correspond to the second degree of mass loss in the TG curves. They are also related to the further stages of polymer decomposition. However, peaks in the range of 440–500°C are most likely related to the polymerization and cross-linking of polymers presented in the samples.[26–29] What is more interesting, as mentioned earlier, peaks above 510°C were observed in the DSC curves only for samples with sodium polyacrylate. There are noticeable differences between samples with raw and pretreated cotton; in the second case, these temperatures are significantly shifted toward higher values, even by 40–50°C, what may indicate better penetration of the used hydrogel mixtures, because the fibers are "open." They can be related to the carbonization of cellulose (about 600°C), which overlaps with the transformations taking place in the used fire retardants, such as decomposition of boehmite to γ-Al_2O_3 (550–800°C), which is an endothermic effect.[30] These peaks are not noticeable for samples with chitosan and sodium alginate, because it is probably related to the degree of degradation of the samples. This is confirmed by the results of the TG measurements (the residue was higher for samples with sodium polyacrylate) (Fig. 7) and fire tests (samples with ANa were covered with intumescence, while samples with CH and SA were more carbonized) (Fig. 4).

PCFC analysis

Figure 8 shows exemplary graphs of HRR as a function of temperature for cotton composite samples impregnated with hydrogels with the addition of composition 3: aluminum hydroxide, zirconium oxide, and glass fibers. Table 4 presents the remaining results of the PCFC analysis, i.e., pHRR and their corresponding temperatures, sumHRC, THR, and residue.

Two HRR peaks were observed for each of the analyzed samples in Fig. 2. The first one occurs in the temperature range of 250–340°C and is characterized by the maximum degree of heat release. In turn, the second peak, in the temperature range of 400–430°C, is

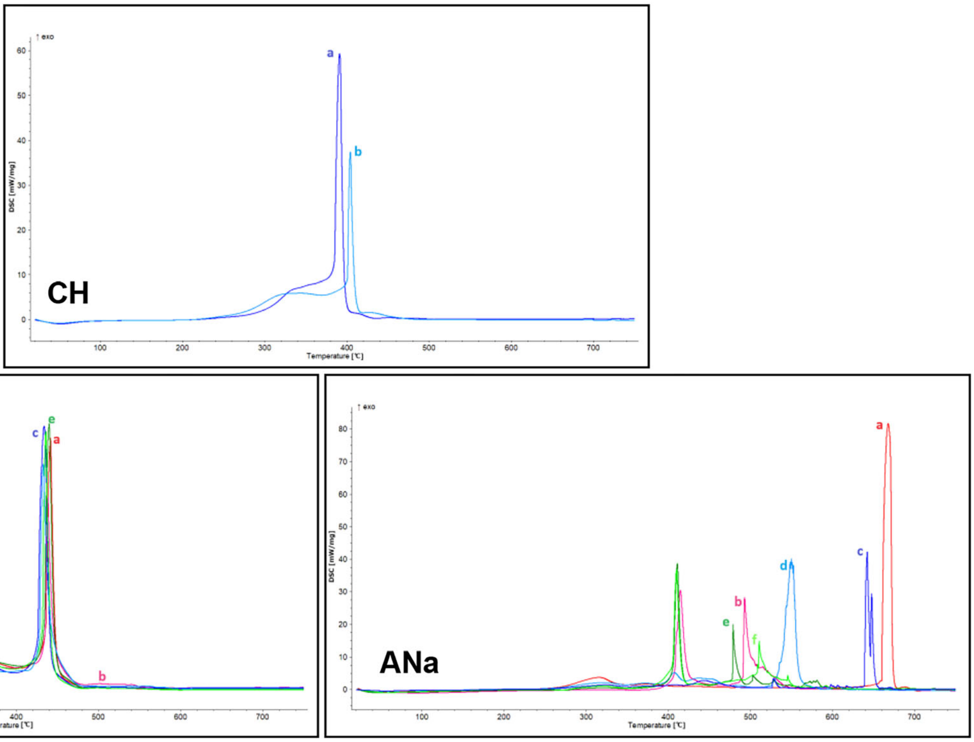

Fig. 5: DSC curves of the selected samples: CH (a-5/CH/PT, b-5/CH/P), SA (a-1/SA/PT, b-1/SA/P, c-5/SA/PT, d-5/SA/P, e-8/SA/PT, f-8/SA/P), and ANa (a-1/ANa/PT, b-1/ANa/P, c-5/ANa/PT, d-5/ANa/P, e-8/ANa/PT, f-8/ANa/P)

very small. Only for samples impregnated with sodium polyacrylate the situation is reversed.

The peaks in the first temperature range are related to the beginning of decomposition process of both, cotton and hydrogels themselves. Compared to the DSC curves, they are shifted toward lower temperatures, where these effects occurred at temperatures of 310–350°C. The protective gas atmosphere in the case of PCFC measurements had an influence on these results. It can also be concluded that samples impregnated with sodium polyacrylate and sodium alginate degrade more slowly, due to the higher degree of coverage, as well as the fact that during contact with temperature, they swell more, creating a protective layer. This is also confirmed by the percentages of residues (Table 4). For the composites with sodium polyacrylate and sodium alginate, they were the highest: respectively, 53.2% and 37.8% for the samples with pure cotton and 36% and 24% for the samples with pretreated cotton. These results also indicate that the pretreatment process negatively affects the thermal properties of the composites. This is also confirmed by the values of the THR and sumHRC parameters, which were higher in the case of samples where the cotton was pretreated with sodium hydroxide solution.

The peaks in the temperature range of 400–430°C are slightly shifted (by 10°C) toward higher temperatures compared to the analysis of DSC curves, where they were only visible for samples with sodium polyacrylate and chitosan. They correspond to the next stage of polymer decomposition.[26–30] The remaining peaks visible on the DSC curves, related to, among others, the transformations of the used fire retardants, disappeared in the case of PCFC curves due to the protective nitrogen atmosphere.

DMA analysis—tension mode

Figure 9 presents the E´ modulus and tan δ graphs at 1 Hz and 20 Hz for samples impregnated with the addition of fire-retardant composition no. 3 ($Al(OH)_3$/ZrO_2/GF). On the other hand, Fig. 10 shows exemplary E´ curves for the 3/ANa/P, 3/CH/P, and 3/SA/P systems at all of the frequencies for both loading cycles. The E´ modulus is the so-called storage modulus, that is, responsible for the ability of the material to store elastic energy. The tan δ coefficient, called the dissipation factor, informs us about the resulting phase shift and illustrates the relationship of the E´ and E´´ moduli (loss modulus): tan δ=E´/E´´. The size of the angle provides information about the amount of elastic and viscous components in the sample. Completely viscous substances exhibit a phase shift of 90º, while completely elastic substances exhibit a phase shift of 0°. For completely viscous substances, the value of the E*-

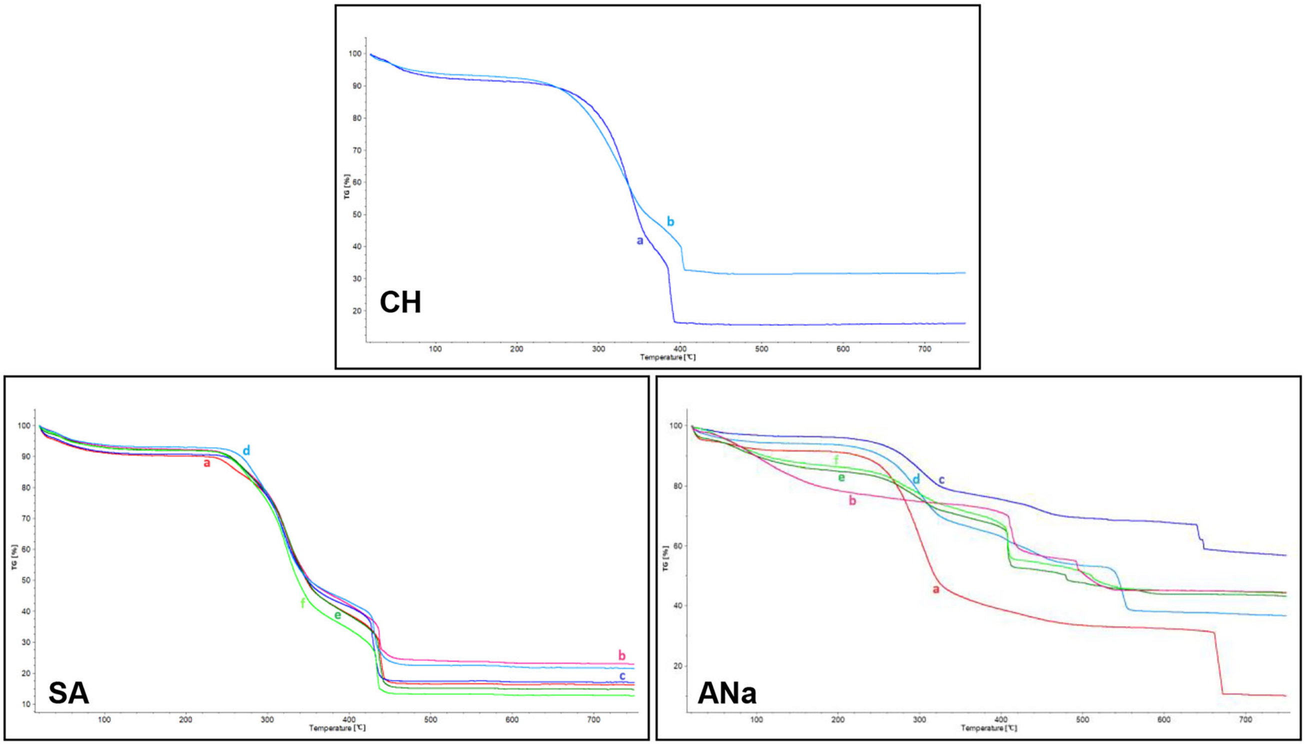

Fig. 6: TG curves of the selected samples: CH (a-5/CH/PT, b-5/CH/P), SA (a-1/SA/PT, b-1/SA/P, c-5/SA/PT, d-5/SA/P, e-8/SA/PT, f-8/SA/P), and ANa (a-1/ANa/PT, b-1/ANa/P, c-5/ANa/PT, d-5/ANa/P, e-8/ANa/PT, f-8/ANa/P)

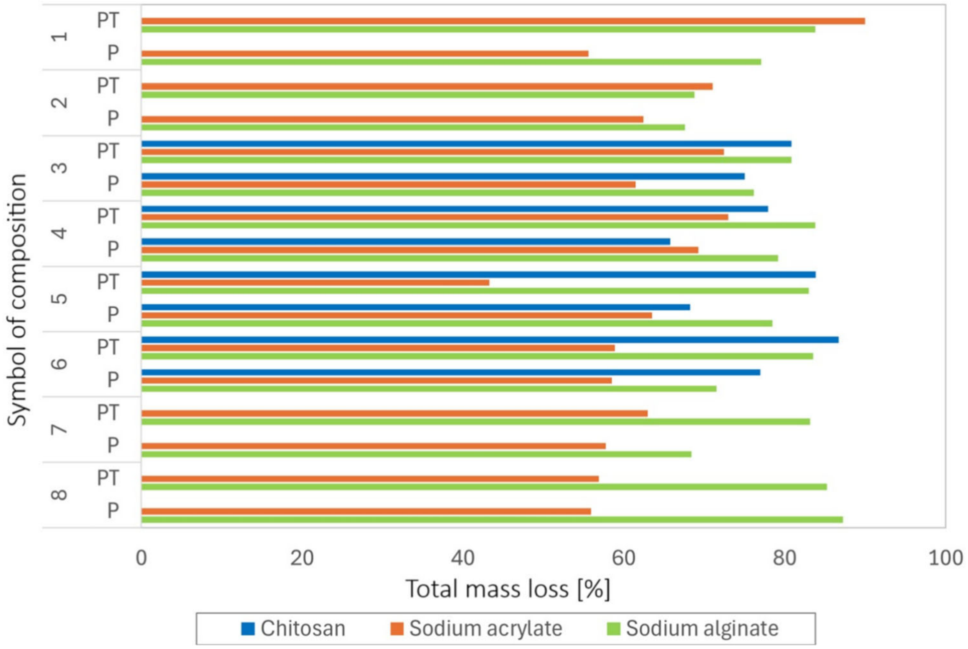

Fig. 7: Total mass loss calculations based on TG curves

complex modulus is equal to the value of the E´´ loss modulus, while for the completely elastic substances, it is equal to the value of the E´ storage modulus.

Comparing the values of the E´ modulus to the frequency, practically no differences were observed for the individual sample. Differences occurred only between subsequent measurements, where in the second cycle, for the same samples, the module values were significantly different from each other, i.e., they were characterized by a higher value. This is confirmed by Fig. 10. It can also be seen that in all cases, except for the compositions with sodium polyacrylate, the E´ modulus value for the samples with pure cotton is significantly higher than for the samples with pretreated cotton (Fig. 9). This means that these composites have higher mechanical strength, regardless of the frequency. Whereas the pretreatment process weakens the fibers in terms of their mechanical strength. In the case of sodium polyacrylate, the higher values can be explained by the fact that the impregnation solution had the appropriate viscosity, what allowed it for precise penetration between the cotton fibers.

In both cycles, as the temperature increases, the E´ modulus value begins to decrease, reaching a minimum in the range of 50°C, and then slowly begins to increase again. In the temperature range of −20°C–50°C samples soften, becoming elastic materials. They are also slightly stretched (Fig. 11). The most stable samples are those with sodium alginate, but they are characterized by the lowest E´ values. In the second temperature range, between 50 and 200°C, the E´ modulus starts to increase again. The movement of the stretched cotton fibers is blocked by the swelling and drying hydrogel, what causes that the material stiffens again and because of that the E´ modulus increases again. This is confirmed by the second measurement cycle. Much stiffer material is subjected to the same loads; therefore, the values of the E´ modulus are higher. This behavior is reflected in the tan δ curves, whose courses indicate significant changes in the material behavior during the measurement, in relation to temperature and frequency. Thanks to this, it can be concluded that this phenomena is a nonlinear viscoelastic behavior. Analyzing the composition of the individual samples, the negative effect of water content in the initial hydrogel solution can also be noticed. Higher water content causes a lower E´ modulus value. Comparing the values of the E´ modulus with the literature data, higher values were obtained than for the separate components.[31–38]

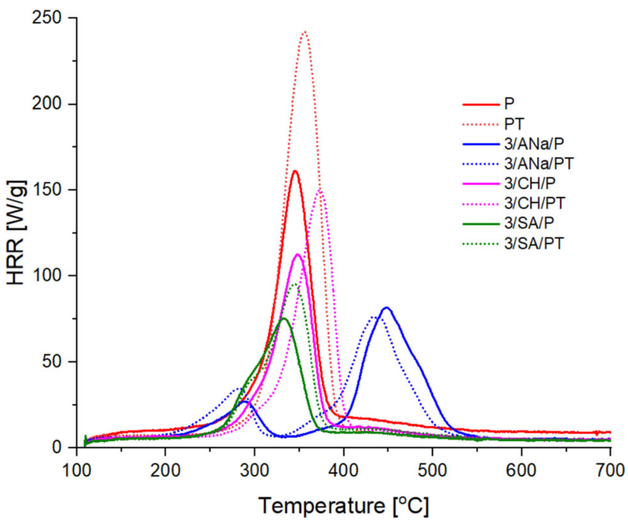

Fig. 8: Heat release rate curves vs temperature for the composite cotton samples impregnated with composition 3: $Al(OH)_3$, ZrO_2, and GF

Figure 12 presents collective graphs of the E´ values for all of the analyzed systems vs selected temperatures, i.e., −50°C, 0°C, 25°C, 100°C, and 150°C for the first loading cycle.

DMA analysis—shear mode

The aim of DMA measurements in the shear mode was to check the adhesion of hydrogel coatings to cotton fabrics. The shear direction was set parallel to the fabric fibers, because like most materials, cotton exhibits anisotropic properties, i.e., its mechanical properties are directional. The measured values of shear modulus G´ for the frequencies of 1 Hz and 20 Hz for samples impregnated with sodium polyacrylate and sodium alginate with the addition of fire-retardant system no. 3 are shown in Fig. 13.

Analyzing the above curves, it was found that the values of the G´ modulus are several times smaller than those of the E´ storage modulus, what is consistent with the literature data concerning the discussed moduli. The E´ modulus is independent of the measurement mode, and therefore, its values should be higher.[39,40]

Table 4: Results of the PCFC measurements

Sample symbol	$pHRR_1$ [W/g]	T_{p1} [°C]	$pHRR_2$ [W/g]	T_{p2} [°C]	sumHRC [J/K g]	THR [J/g]	Residue [%]
P	161	313	17	430	199	10,3	5
PT	241	320	9	421	272	11,6	2,5
3/ANa/P	27	255	82	411	120	7,4	53,2
3/ANa/PT	34	254	76	398	120	7,6	36
3/CH/P	112	315	12	430	138	7,0	27,7
3/CH/PT	149	337	9	427	176	8,1	26,7
3/SA/P	75	300	9	424	93	5,7	37,8
3/SA/PT	95	309	11	430	117	6,7	24

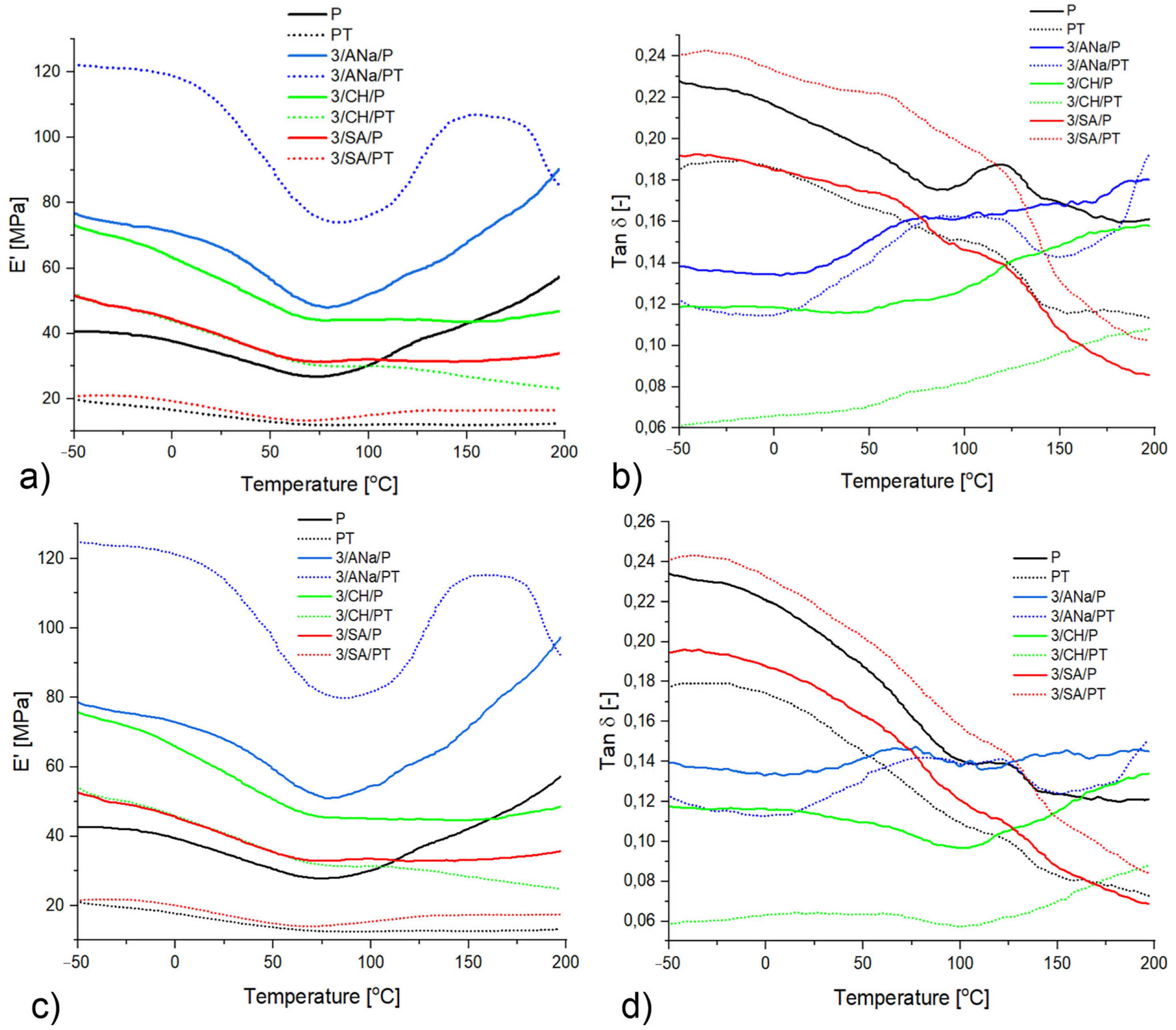

Fig. 9: Dependence of the E´ modulus and the tan δ phase shift angle on the temperature for samples with fire retardant system no. 3: (a) E´ at a frequency of 1 Hz, (b) tan δ at a frequency of 1 Hz, (c) E´ at a frequency of 20 Hz, and (d) tan δ at a frequency of 20 Hz

In the case of DMA measurement in the shear mode, there are also significant differences between the G´ modulus values for pure and pretreated cotton. The same relationship occurs here as in the tension mode, where for sodium polyacrylate, the corresponding modulus values were higher for the pretreated cotton system, while for sodium alginate, these values were higher for the pure cotton system. The course of the curves also indicates that above 50°C, the mechanical properties of the composites deteriorate because the G´ modulus value drops significantly. In the case of samples with sodium polyacrylate, significant fluctuations appear in the graphs above 100°C (pure cotton) and 150°C (pretreated cotton), what indicates swelling of the tested systems. This effect was not observed for samples with sodium alginate. It can also be stated that they are less susceptible to shearing because they are characterized by higher G´ values.

SEM analysis

Figure 14 shows SEM microphotographs of the samples impregnated with composition number 5 (ZrO_2, GF, and MF) before and after the fire test.

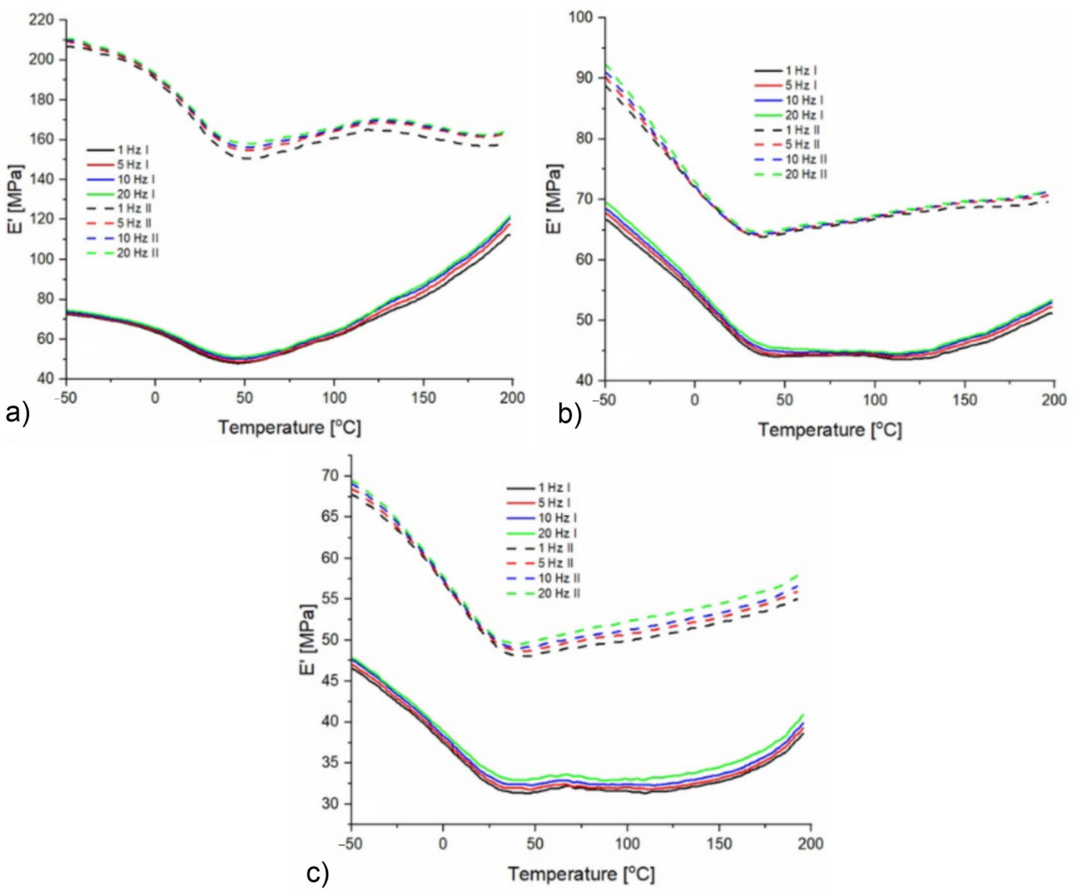

Fig. 10: Dependence of the E´ modulus on the frequency for the 3/ANa/P (a), 3/CH/P (b), and 3/SA/P (c) systems (I–first cycle and II–second cycle)

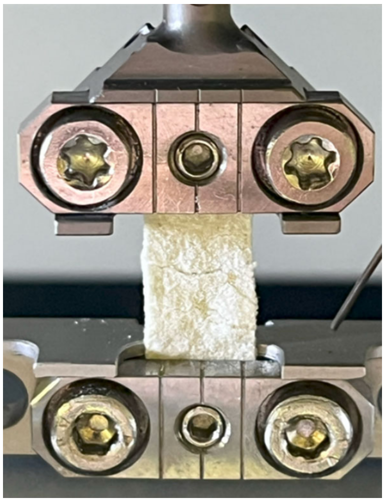

Fig. 11: Exemplary sample after the DMA test in tension mode

In most of the SEM microphotographs of the samples with sodium alginate before the fire test, regardless of the fabric preparation or the used composition of the fire retardants, a compact and uniform structure with embedded glass/mineral fibers or undissolved ceramic fire-retardant particles was observed, which after the fire test transformed into highly porous pumice. This is related to the viscosity of the sodium alginate solution, which was the highest among the analyzed hydrogel solutions, and did not allow for deep penetration of the cellulose fibers. However, in the case of the SEM microphotographs of the samples with sodium polyacrylate after the fire test, an intumescent broccoli-type structure was observed in most cases, what was previously confirmed in photographs of these samples immediately after the fire test (Fig. 4). Only when comparing the appearance of the samples with chitosan before the fire test, no major differences were noticed, i.e., hydrogel structures covering the fabric (only precipitations of the fire retardants contained in the impregnation mixtures). However, after the fire test, fragmentary delamination

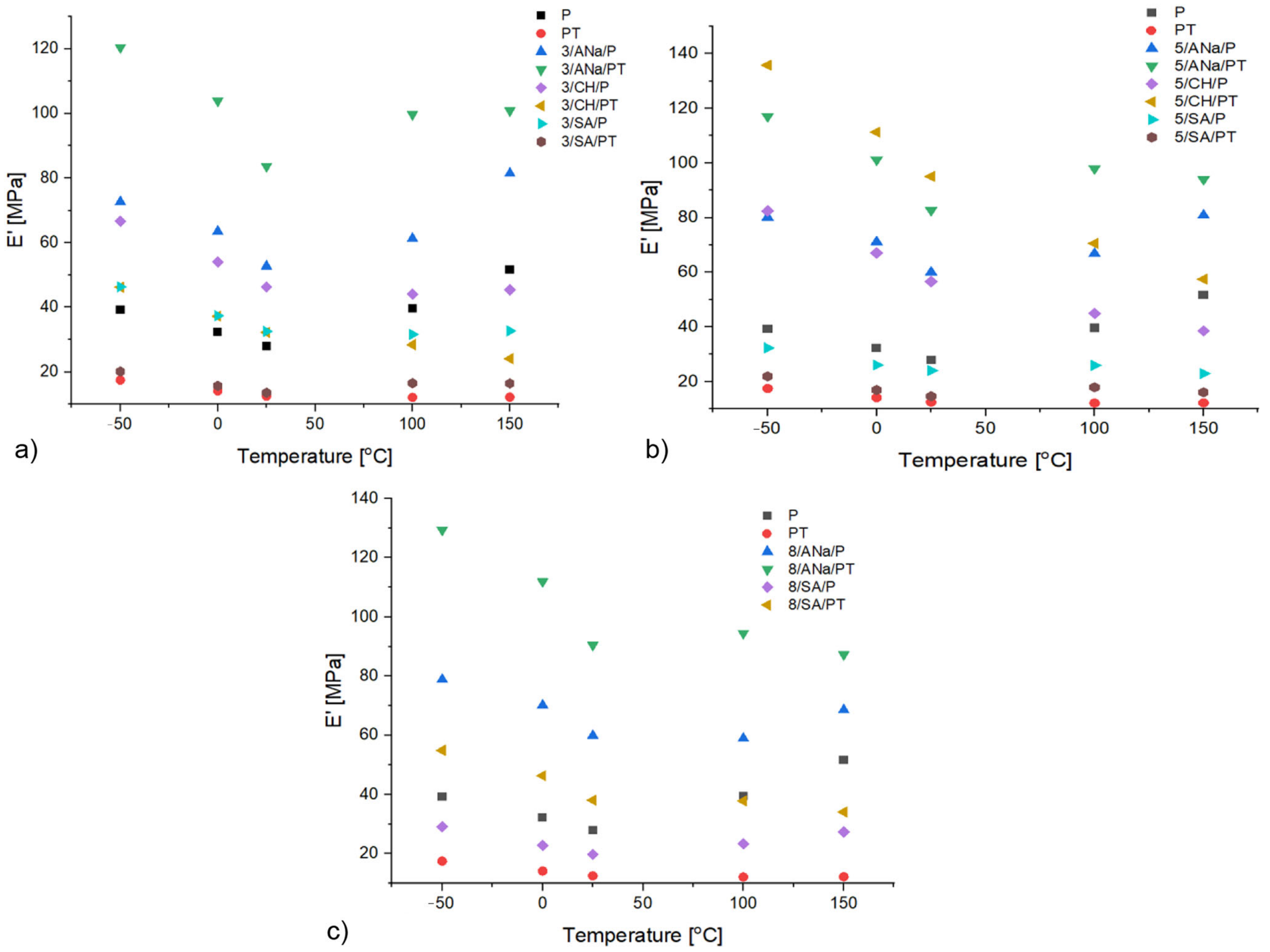

Fig. 12: E´ modulus vs temperature: (a) fire-retardant system no. 3, (b) fire-retardant system no. 5, and (c) fire-retardant system no. 8

could be observed, indicating that the hydrogel/fabric had burned out.

IR analysis

The aim of MIR spectroscopic measurements was to check/confirm what substances degraded during the fire test, so it will be possible to determine the mechanism of the fire-retardant effect of the hydrogel with the addition of the selected fire retardants. Comparing the MIR spectra before and after the fire test, it was noticed that some of the bands completely disappeared, mainly in the 3500–2000 cm^{-1} area, while in the other areas, a large part of the bands lost their intensity, what indicates the complete or partial removal of some functional groups from the tested samples, mainly in the polymer and cellulose chain (Fig. 15). It should be mentioned here that the structural analysis of the spectra was difficult, because the bands coming from cellulose, i.e., the main component of cotton fabric, overlapped with the bands coming from the used hydrogels. Additionally, metal ions contained in fire retardants caused shifts in the bands and changes in their shape. However, no major differences were found between the spectra of the used cotton fabric, i.e., pure or pretreated.

The broad band with a maximum at approximately 3400 cm^{-1} comes from the stretching vibrations of the OH– group, and in the case of chitosan, it may overlap with the stretching vibration of the N–H group. For samples after the fire test, this band significantly loses intensity and width, but does not disappear completely, what indicate incomplete removal of water from the tested samples. The band at 2900 cm^{-1} corresponds to the stretching vibrations of the –CH$_2$– group in the polymer chain, such as symmetric or asymmetric stretching vibrations of –CH$_2$– in the pyranose ring of chitosan. It may also be a band originating from the stretching vibrations of the C–H group in the glucose

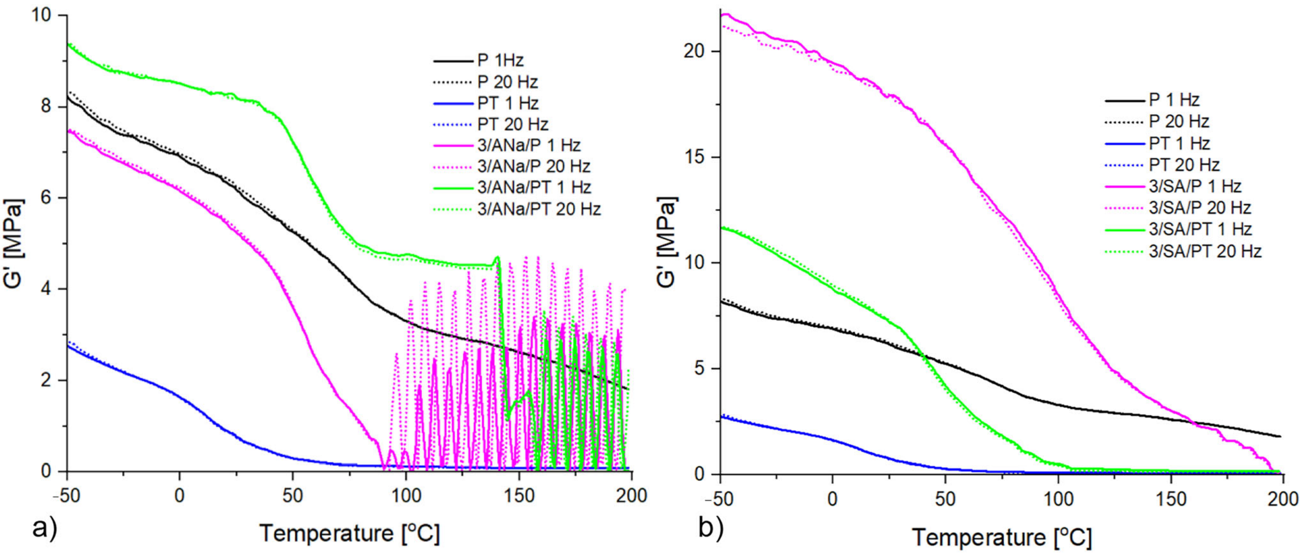

Fig. 13: G´ modulus vs temperature for the samples with: (a) sodium polyacrylate and (b) sodium alginate

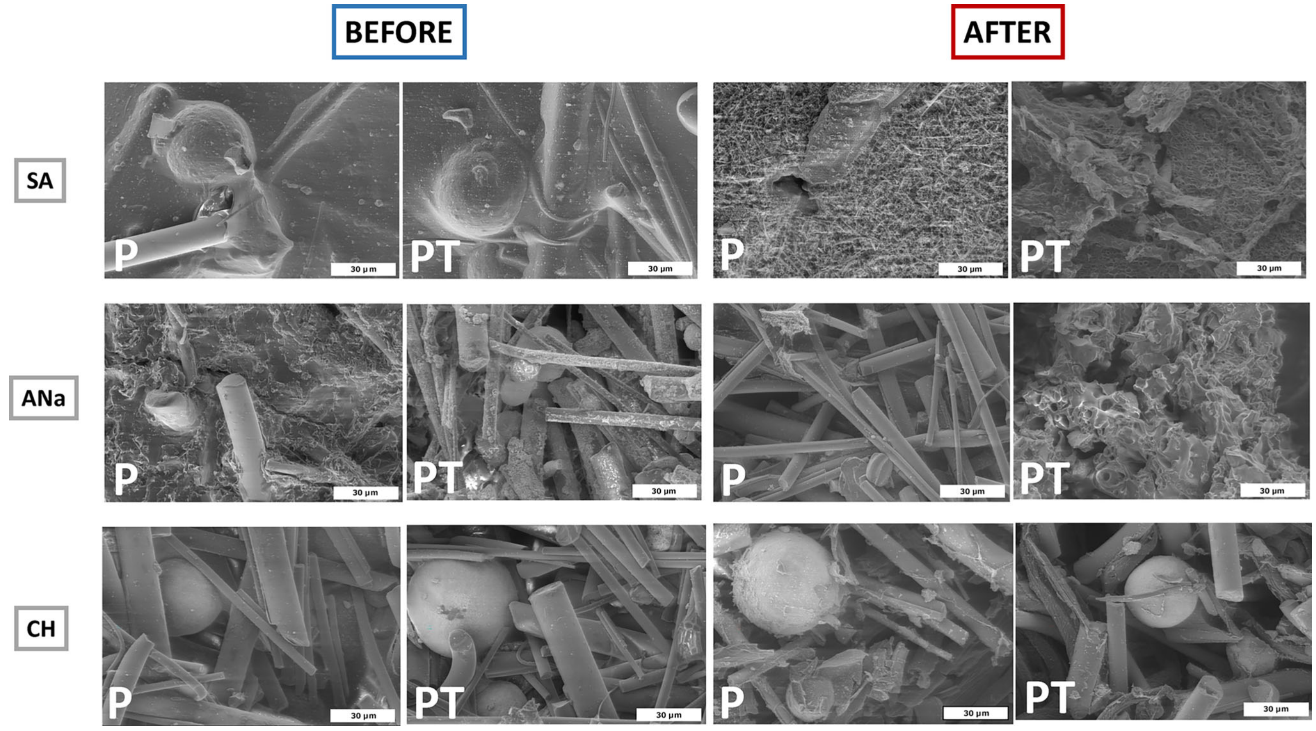

Fig. 14: SEM microphotographs of the samples impregnated with composition number 5 (ZrO_2, GF, and MF) before and after the fire test (upper row: 5/SA/P, 5/SA/PT; middle row: 5/ANa/P, 5/ANa/PT; and bottom row: 5/CH/P, 5/CH/PT)

unit in cellulose. For ash samples, this band practically disappeared in all cases. The bands at 2540 cm^{-1} and 2330 cm^{-1} were present only in samples with sodium polyacrylate, and they corresponded to the valence vibrations of –CO_2– groups in the polymer chain. They disappeared completely after the fire test. A sharp and medium-intensity band at approximately 1570 cm^{-1} was present in all of the tested samples before the fire test, but it became flattened in the spectra of the corresponding ashes. It can be the N–H deformation

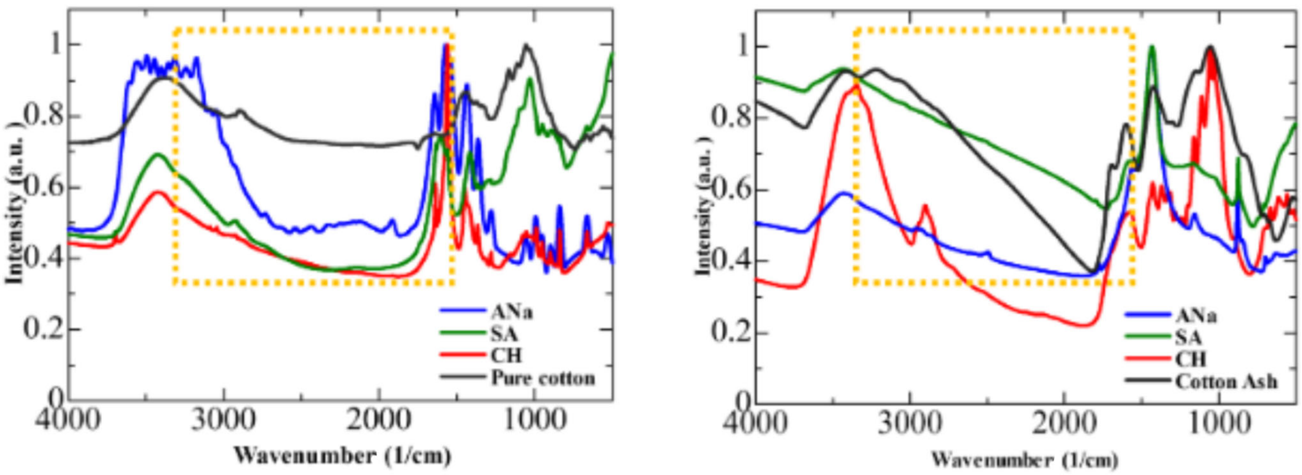

Fig. 15: **MIR spectra of the pure cotton samples impregnated with composition number 5 (ZrO_2, GF, and MF) before (on the left) and after the fire test (on the right) (blue curve: sample 5/ANa/P, green curve: sample 5/SA/P, red curve: sample 5/CH/P, and gray curve: pure cotton)**

vibration in the case of chitosan, stretching vibrations of asymmetric and symmetric bands of carboxylate O–C–O asymmetric anions in sodium alginate, or symmetrical stretching vibrations of carboxyl anions –COO– in sodium polyacrylate. The band at 1440 cm^{-1} is present in all of the tested samples, before and after the fire test. It may correspond to the C–O stretching vibrations in alcohol groups or to symmetric or asymmetric $–CH_2–$ stretching vibrations in the chitosan pyranose ring. This band is also attributed to the stretching vibrations of asymmetric and symmetric bands of the $R–COO^-$ anions. Band at 1280 cm^{-1} also corresponds to these vibrations, with the difference that in most spectra of the corresponding ashes, it has disappeared or is very poorly visible. Band at 1170 cm^{-1} is assigned to the vibrations of the C–O and C–O–C glycosidic bonds in the chitosan polymer chain and the –C–O– groups of secondary alcohols and ethers functions existing in the cellulose chain backbone, respectively. These bonds are also visible at 1050 cm^{-1} and become less intense with ashes. Bands at 990 cm^{-1} and 870 cm^{-1} are assigned to the C–O stretching vibration in uronic acid and α-L-gulopyranuronic asymmetric ring vibration, mannuronic acid residues in sodium alginate, or absorption band of β-glycosidic linkage between glucose units in cellulose, respectively. As in the previous case, they lose their intensity in ash samples.[41–46]

Summary

The article presents the results of obtaining a new type of the composite hydrogel based on the natural polysaccharides and vinyl derivative doped with ceramic fire retardants, which can be an impregnating mixture to protect cotton fabrics against the fire. Three types of hydrogels, i.e., sodium alginate, chitosan, and sodium polyacrylate, as well as the following fire retardants: magnesium hydroxide, aluminum hydroxide, zirconium oxide, mineral fibers, and glass fibers, were tested. In order to obtain the highest possible degree of impregnation, the method of applying hydrogel by immersion was chosen. Additionally, for comparison purposes, a pretreatment procedure was applied to cotton fabric using an 18 wt% aqueous sodium hydroxide solution. These treatments allowed to obtain durable hydrogel/fabric composites with varying degrees of fire resistance. Based on the results of TG/DSC thermal analysis measurements, reaction to fire tests, and SEM micrographs, it was found that composites with pretreated cotton are more resistant to fire because the impregnating mixture better penetrates the so-called "open" cellulose fibers. Based on the obtained test results, it was also found that the lower the initial viscosity of the mixture, the higher the degree of impregnation. Therefore, the best results were obtained for samples with sodium polyacrylate. They also showed the highest degree of intumescence during the contact with fire and were characterized by the fastest self-extinguishment after removing the flame. Comparing the compositions of the fire-retardant additives, the best results were achieved when magnesium hydroxide was included in the mixture. The above analysis was also confirmed on the basis of the MIR spectra before and after the fire test, where most of the bands "remained" in the spectrum of the sample with sodium polyacrylate. Results of the PCFC tests confirmed the fact that samples with polyacrylate hydrogel degrade slower. They also showed that pretreated cotton degrades a little bit faster than pure cotton material. In turn, thermomechanical tests using the DMA method have shown that the pretreatment process reduces the mechanical strength of the composites due to the weakening of the fibers. Only in the case of the samples with sodium polyacrylate, this effect was opposite.

Summarizing the analysis of MIR spectra with the results of fire tests and SEM microphotographs, it can be concluded that the developed fire-retardant hydrogels fulfill their function well, because under the influence of expansion and the action of fire retardants, they create a kind of passive layer that does not allow complete combustion of the fabric inside.

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Conflict of interest The authors report that there are no competing interests to declare.

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