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Influence of External Factors on the Behavior of Polymer Materials Based on Polyethylene Glycol Maleate

This study aims to evaluate the effect of external physicochemical factors on the behavior of hydrogels based on polyethylene glycol maleate (p-EGM) and to assess their potential applicability in sorption-active polymer matrices and biomedical hydrogel systems. This paper presents the results of an investigation into the physicochemical properties of polyethylene glycol maleate and acrylamide solutions in acrylic acid and their cured products. The degree of unsaturation of the initial unsaturated polyester was determined using the bromide–bromate method. The dynamic viscosity of the initial polymer–monomer mixtures was found to be in the range of 0.251–0.697 Pa·s, while the density of the solutions varied from 1.0554 to 1.0996 g/cm³. The density of the cured terpolymers was calculated by the hydrostatic method, and the calculated total volumetric shrinkage did not exceed 15 %. The composition of the obtained terpolymers was confirmed by HPLC analysis. The synthesized hydrogels exhibited a high swelling degree (up to 2898 %) and pronounced sensitivity to environmental pH (4–8) and temperature (35–39 °C), as established by gravimetric measurements. Structural identification was performed using IR and NMR spectroscopy, and the surface morphology was analyzed by SEM. It was demonstrated that an increased acrylic acid content leads to the formation of a more porous polymer network with enhanced water absorption, controllable permeability and structural stability, indicating potential biomedical applicability of the developed materials. Overall, the obtained results suggest that the synthesized hydrogels may be considered promising candidates for potential use in sorption-active polymer matrices and hydrogel-based wound dressing systems.

Keywords: unsaturated polyester, terpolymer, hydrogel, “cold” curing, external factors, water absorption, swelling degree, acrylic acid, polyethylene glycol maleate.

Introduction

Hydrogels are unique polymeric materials capable of retaining large amounts of water. This property makes them highly attractive for medical applications, including wound and burn treatment, as well as controlled drug delivery systems [1–3]. Due to their three-dimensional mesh structure, swollen hydrogels maintain optimal moisture levels, regulate the diffusion of active compounds and gas exchange, and protect damaged tissues from secondary infection [4, 5]. In addition, the ability of such materials to mimic the physicochemical properties of the extracellular matrix ensures their biocompatibility and contributes to the acceleration of tissue healing and regeneration processes [6].

Structural modification of polymer hydrogels allows their properties to be precisely tuned and enables the materials to perform targeted physiological functions [7]. The introduction of functional groups capable of ionization, thermosensitive or biocompatible segments into the polymer network allows the creation of materials with adjustable parameters of swelling, mechanical strength, moisture transfer and sorption activity [8]. Such modifications make it possible to adapt hydrogels to specific physiological conditions: regulating moisture in the wound coverage area, increasing sorption capacity during exudation or, conversely, retaining moisture in dry wounds [9].

Regulating the density of cross-linking and the composition of the polymer mesh allows control not only over mechanical properties, but also over the kinetics of active substance release [10]. In particular, looser networks with low cross-linking density ensure rapid release of drug compounds and effective sorption of exudate, while dense structures with a higher degree of cross-linking ensure prolonged release and stability

of form [11]. Thus, varying the degree of swelling, porosity, and elasticity makes it possible to adapt hydrogels to specific clinical tasks, including the treatment of burns, trophic ulcers, postoperative and chronic wounds [12, 13].

It is worth noting that modern research is focused on creating functional and stimulus-sensitive hydrogels capable of responding to external physicochemical factors — pH, temperature, ionic strength, light radiation or mechanical impact — and ensuring targeted drug release [14, 15]. Such “smart” materials change their degree of swelling and permeability in response to external stimuli, which makes it possible to accurately dose and spatially and temporally control the therapeutic effect [16].

Particular attention is paid to thermo- and pH-sensitive systems that function under conditions close to physiological conditions. Hydrogels that exhibit reversible “swelling-collapse” transitions at a temperature of ~35–39 °C and in the pH range of 5–8 are most promising for use as gel dressings and transdermal delivery systems. At body temperature (~37 °C), such materials can partially collapse, releasing moisture to the damaged surface and preventing over-moisturization, and when the acidity characteristic of an inflamed environment changes, they can swell again, actively absorbing exudate.

In addition, structural modification of such hydrogels allows additional functional components to be incorporated into their network, such as antiseptics, antibiotics, anti-inflammatory drugs, and metal or oxide nanoparticles to impart antibacterial properties [4, 8]. Thus, current trends in the development of polymer hydrogels are aimed at creating multifunctional adaptive materials that not only provide a comfortable moist environment and tissue protection, but are also capable of actively participating in the healing process [9, 14].

Taken together, these features make modified hydrogels a promising class of polymer systems for medicine and biotechnology. They can serve not only as a material for wound dressings, but also as a basis for intelligent local therapy systems, biosensors, cell matrices, and soft implants of a new generation [6, 15].

Despite significant progress in the development of polyethylene glycol maleate-based hydrogel systems, the combined effect of ionogenic acrylic acid and non-ionogenic acrylamide on the structure formation and stimulus sensitivity of polyethylene glycol maleate networks remains insufficiently clarified [6, 14]. In particular, the balance between polyelectrolyte swelling provided by acrylic acid and the hydrogen-bond-driven structuring introduced by acrylamide requires further systematic investigation. Understanding this interplay is essential for the rational design of hydrogels with controlled responsiveness under physiologically relevant conditions.

Compared to our previous studies focused primarily on related polyethylene glycol maleate systems, the present work provides a systematic investigation of ternary p-EGM–AA–AAm networks with controlled variation of ionogenic and non-ionogenic fragments. This approach makes it possible to elucidate the combined effect of electrostatic and hydrogen-bond interactions on the responsive behavior of the hydrogels under physiologically relevant conditions.

In view of this, systems based on terpolymers of unsaturated polyesters with vinyl monomers [17, 18], which combine hydrophilicity [19], biocompatibility and the ability to immobilize drug compounds [20], are of particular interest. Due to the presence of reactive double bonds, such systems are easily modified and allow varying the degree of cross-linking [21], and therefore controlling the swelling rate, porosity and stability of the hydrogel [22]. Such materials demonstrate high moisture retention capacity and structural stability, which is particularly important for dressings that are in prolonged contact with biological tissues [2, 7, 12].

In this regard, the present study is focused on elucidating the influence of external physicochemical factors on the behavior of hydrogels based on polyethylene glycol maleate–acrylic acid–acrylamide terpolymer systems obtained by “cold” curing. The novelty of this work lies in the systematic investigation of the relationship between monomer composition, network structure, and the responsive swelling behavior of the resulting hydrogels under physiologically relevant pH and temperature conditions. The main objective of the study is to establish the physicochemical regularities governing the formation, morphology, and stimulus sensitivity of the synthesized materials in order to assess their suitability for use in sorption-active polymer matrices and flexible hydrogel patch applications.

Experimental

The experimental work was carried out using the following reagents (“Sigma-Aldrich”, USA):

– for the synthesis of the starting unsaturated polyester — polyethylene glycol maleate (p-EGM) — by polycondensation reaction: ethylene glycol and maleic anhydride; zinc chloride (catalyst for the synthesis);

- for the synthesis of p-EGM-based terpolymers: acrylic acid (AA, which is both a co-reagent and a solvent), acrylamide (AAM);
- for “cold” curing of the triple systems under study: an initiating system consisting of benzoyl peroxide (BP, initiator) and dimethylaniline (DMA, activator);
- for determining the molecular weight of p-EGM and washing the terpolymers after synthesis: dioxane (solvent).
- to study the effect of pH on the behaviour of the synthesized gels: buffer solutions with pH values from 4.0 to 8.0.

All reagents had a purity of 99.95 % and were used without additional purification.

The synthesis of the starting unsaturated polyester (p-EGM) was carried out by polycondensation of ethylene glycol with maleic anhydride in the presence of a zinc chloride catalyst (0.2 % of the mass of the reaction mixture). The ratio of reagents in the reaction mixture was 1.05:1.0 mol. Polycondensation was carried out according to the standard method [21]. The yield of the resulting polyester was 98 %. The molecular weight of p-EGM was determined using a VISCOTEK 270 DUAL DETECTOR gel permeation chromatograph (MALVERN Panalytical Ltd., UK) equipped with a four-capillary bridge viscometer detector and low-angle/right-angle light scattering detectors (LALS/RALS) using a 3 mW laser with a wavelength of 670 nm. Dust-free dioxane was used as the solvent. The molecular weight of the synthesized p-EGM was ~1232 Da (M_w).

In order to obtain polymer gels, solutions with different ratios of p-EGM, AA and AAM components were prepared: ~15:70:15 wt.%, 15:50:35 wt.% and 15:35:50 wt.%. The dynamic viscosity of the obtained solutions ($T = 293$ K) was measured using an SV-10 vibration viscometer (A&D Company, Japan) operating on the tuning fork vibration principle at 30 Hz. The instrument was equipped with a VT3 thermostat bath (TERMEX, Russia) with a capacity of 3 L and a temperature control range of +20 °C to +200 °C to ensure temperature stability during measurements. The density of the solutions was measured by the pycnometric method in accordance with ISO 1675:1985.

“Cold” curing was carried out using an optimised initiating system consisting of 1.0 wt.% benzoyl peroxide (initiator) and 0.15 wt.% dimethylaniline (activator) relative to the total mass of the reaction mixture. The polymerization process was carried out at 293 K.

The resulting p-EGM-AA-AAM terpolymers were washed with dioxane to remove unreacted residues. The mother liquors were analysed by high-performance liquid chromatography (HPLC) using an LC-20 Prominence system (Shimadzu, Japan) equipped with an SPD-20A UV-Vis absorbance detector and an SPD-M20A diode array detector. The results were used to determine the actual composition of the synthesised terpolymers. The yield of the products was calculated by gravimetric analysis.

The identification of the curing products was carried out by IR and NMR spectroscopy to establish the presence of characteristic functional groups. IR spectra were recorded in KBr pellets on an FSM 1201 spectrometer (Infraspek, Russia) with a spectral range of 400–7800 cm^{-1} and a pyroelectric detector module (LiTaO_3), and ^1H NMR spectra were recorded on a DX-90M instrument (Xiamen Dexing Magnet Tech. Co., Ltd., China) operating at a ^1H resonance frequency of 90 MHz with a resolution of 1 Hz.

The density of the cured terpolymers was evaluated by the hydrostatic method (ASTM D792-13). The volumetric shrinkage of terpolymers was calculated based on experimental values of the density of the initial solutions and cured samples, according to formula (1):

$$S_v = \frac{\rho_d - \rho_l}{\rho_l} \cdot 100 \%, \quad (1)$$

where ρ_l — initial density of the solution, g/cm^3 ; ρ_d — density of the cured dry sample, g/cm^3 .

The morphology of the polymer surface was studied using SEM on a MIRA 3 microscope (TESCAN, Czech Republic) at an accelerating voltage of 5.0 kV with an SE detector and a magnification of 57.6–57.7 thousand times (resolution 1024×1024 pixels).

The hydrophilicity of the cured materials was evaluated by the gravimetric method. The degree of swelling was measured after exposing a sample (~0.5 g) to water at 20 °C (pH 7) for 24 hours. The calculation was performed using formula (2):

$$\alpha = \frac{m - m_0}{m_0} \cdot 100 \%, \quad (2)$$

where m — mass of the swollen sample, g; m_0 — dry sample mass, g.

The study of the influence of external factors on the behavior of synthesized hydrogels was carried out in the pH range of 4–8 and at a temperature of $T = 35\text{--}39\text{ }^{\circ}\text{C}$ using the gravimetric method. The calculation was performed using formula (2).

The temperature at which thermal deformation began was determined by TGA using the Labsys Evolution TG-DTA/DSC synchronous thermal analysis system (Setaram Instrumentation, France) with an operating temperature range up to $1600\text{ }^{\circ}\text{C}$.

All measurements were performed in triplicate ($n = 3$). The experimental data are presented as mean \pm standard deviation. Statistical analysis included calculation of the arithmetic mean, standard deviation, and relative error using standard descriptive statistical methods.

Results and Discussion

For a systematic study of the physicochemical properties of hydrogel materials, three solutions based on p-EGM, AA, and AAm monomers were prepared in the first stage of the research. The ratios of 15:70:15 wt.%, 15:50:35 wt.%, and 15:35:50 wt.% were deliberately chosen to form systems that differ in the concentration of ionogenic fragments, the degree of hydration, and the nature of interchain interactions. Due to the variable content of AA and AAm, the polymer networks differed in the number of potential centers of electrostatic association, hydrogen bonding and the formation of hydrated domains — all these factors influence the viscosity of solutions, the swelling mechanism and the morphology of the final products — gels.

After preparation, the initial solutions were thoroughly homogenized until an optical clarity was achieved in all samples. At this stage, the primary organization of intermolecular contacts — hydrogen bonds, ion-dipole associations and hydration interactions — was established. The degree of optical homogeneity served as an important criterion for the absence of microphase separation and was critical for the further correct formation of the gel structure. After exposure, the system reached a pre-equilibrium configuration in which weak associative interactions stabilized and determined the conditions for the further curing process [18, 21].

After reaching the equilibrium configuration of the initial solutions using an SV-10 vibrating viscometer and a pycnometer, the dynamic viscosity and density values of the analyzed solutions were determined. The results are presented in Table 1.

Pycnometric determination of density showed a steady trend towards a decrease in the mass-volume density of solutions as the proportion of AA increased. Although the differences were small, their reproducibility confirmed the correctness of the observed pattern. Thus, an increase in the AA content in the initial mixture from ~35 wt.% to ~70 wt.% led to a decrease in the density of the solutions from 1.0996 g/cm^3 to 1.0554 g/cm^3 . These differences can be explained by the fact that AA forms less compact intermolecular structures compared to the more polar and intensely intermolecularly interacting components p-EGM and AAm [17]. An increase in AA content leads to a weakening of interfragment associations in the liquid mixture, which is reflected in a slight increase in free intermolecular space and a decrease in density (Table 1).

Table 1

Physical and chemical properties of initial solutions of p-EGM (M_1) with AA (M_2) and AAm (M_3) $T = 293\text{K}$

Composition of prepared solution, wt.%			Density of solution value (ρ_l), g/cm^3	Dynamic viscosity value (η), Pa·s
M_1	M_2	M_3		
15.12	70.29	14.59	1.0554 ± 0.0528	0.251 ± 0.013
15.21	50.41	34.38	1.0787 ± 0.0539	0.417 ± 0.021
15.15	34.86	49.99	1.0996 ± 0.0550	0.697 ± 0.035

Rheological studies have revealed a similar trend: a solution with a higher AA content exhibits lower dynamic viscosity. In particular, a solution with the maximum AA content (~70 wt.%) has the lowest dynamic viscosity η , which is $0.251\text{ Pa}\cdot\text{s}$. Reducing the AA content in the solution to ~35 wt.% leads to an increase in its dynamic viscosity to $0.697\text{ Pa}\cdot\text{s}$. This is due to the fact that the presence of AA reduces the degree of intermolecular adhesion in p-EGM–AA–AAm mixtures and decreases the probability of branched associates forming. Thus, changes in density and dynamic viscosity are consistent with each other and reflect the same structural phenomenon — different degrees of intermolecular organization of components in a liquid mixture

before gel formation occurs. It is worth noting that such differences in rheological characteristics determine the further kinetics of gel formation and the degree of accessibility of reactive fragments.

The introduction of a “cold” curing initiation system ensures copolymerization of the components under identical conditions. This allows the differences in the properties of the final gels to be unequivocally attributed exclusively to differences in chemical composition due to different co-reagent contents in the initial mixture. After the reaction was complete, the resulting hydrogels demonstrated high transparency and homogeneity, confirming the absence of macrophase separation and the effectiveness of terpolymerization. A schematic representation of the terpolymerization reaction is shown in Figure 1.

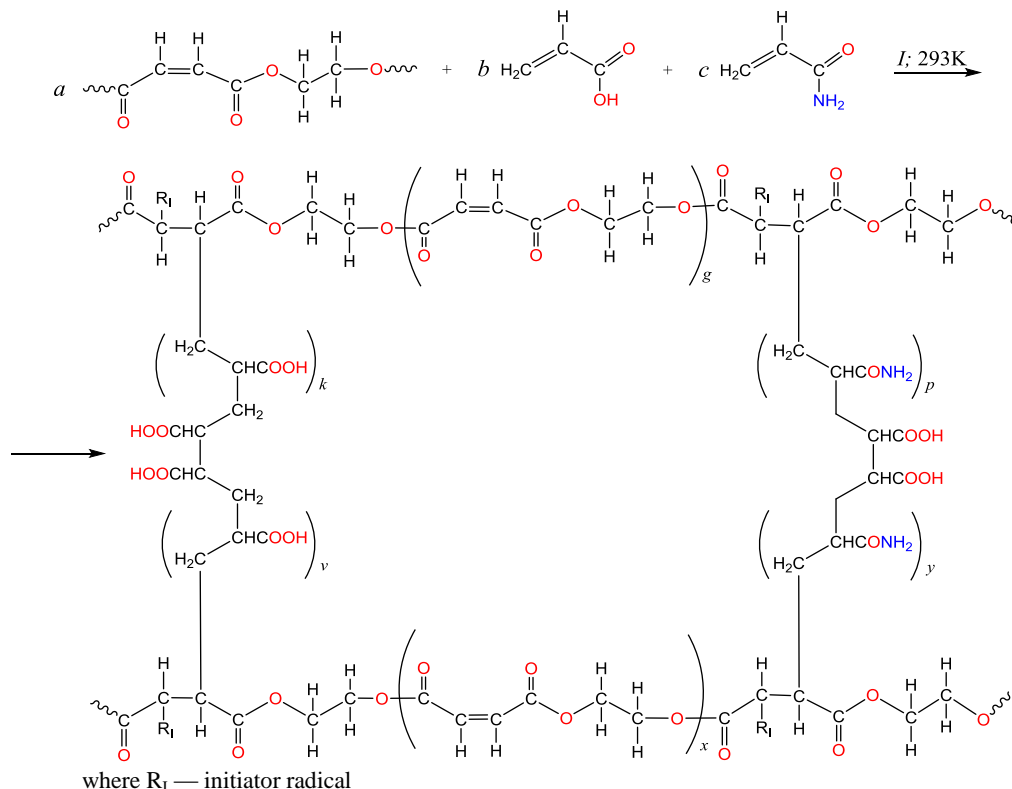


Figure 1. Terpolymer structural fragments of the p-EGM-AA-AAm

The synthesized terpolymers were then washed with dioxane and dried in an oven at $T = 293$ K until a constant mass was achieved. The yield of terpolymers is shown in Table 2. Using HPLC analysis of the mother liquors of the cured products in dioxane, the actual monomer content was found to correspond to the theoretical content. The results are also shown in Table 2. Determining the actual composition ensures correct interpretation of the differences between the synthesized gels, which are due to the different compositions of the initial reaction mixture.

Table 2

**Dependence of terpolymers composition and other of their parameters
on the composition of initial mixtures of p-EGM (M_1)-AA (M_2)-AAm (M_3)**

Composition of the initial mixture, wt. %			Composition of the terpolymers, wt. %			Yield, %	Swelling degree (P), %
M_1	M_2	M_3	m_1	m_2	m_3		
15.12	70.29	14.59	13.9	72.2	13.9	90.4	2898
15.21	50.41	34.38	14.1	52.5	33.4	89.1	2114
15.15	34.86	49.99	15.4	35.8	48.8	88.7	1735

The data presented in Table 2 show that an increase in the acrylic acid content in the terpolymer leads to an increase in the degree of swelling from 1835 % (at the minimum AA content) to 2898 % (at its maximum value). Although AAm is also characterized by a high hydration capacity, its contribution is limited by local hydrogen interactions, which create predominantly compact hydrated regions.

Unlike AAm, AA forms regions with an increased concentration of negative charges in the network after partial dissociation. The accumulation of charge causes electrostatic repulsion between the anionic carboxylate groups within the polymer network, increasing the distance between the chains and leading to a significant expansion of the gel volume. At the same time, the resulting excess osmotic pressure promotes further water penetration into the porous structure and the formation of a powerful hydrate shell around the ionogenic fragments.

Thus, the main factor in the increase in the degree of swelling is the polyelectrolyte effect of AA, which provides significantly stronger osmotic swelling compared to the neutral amide groups of AAm [17].

IR spectroscopic analysis of dried samples allowed us to evaluate the degree of completion of the terpolymerization process. The corresponding IR spectra of the initial p-EGM and terpolymers with compositions of 13.9:72.2:13.9 wt.% and 15.4:35.8:48.8 wt.% are shown in Figure 2.

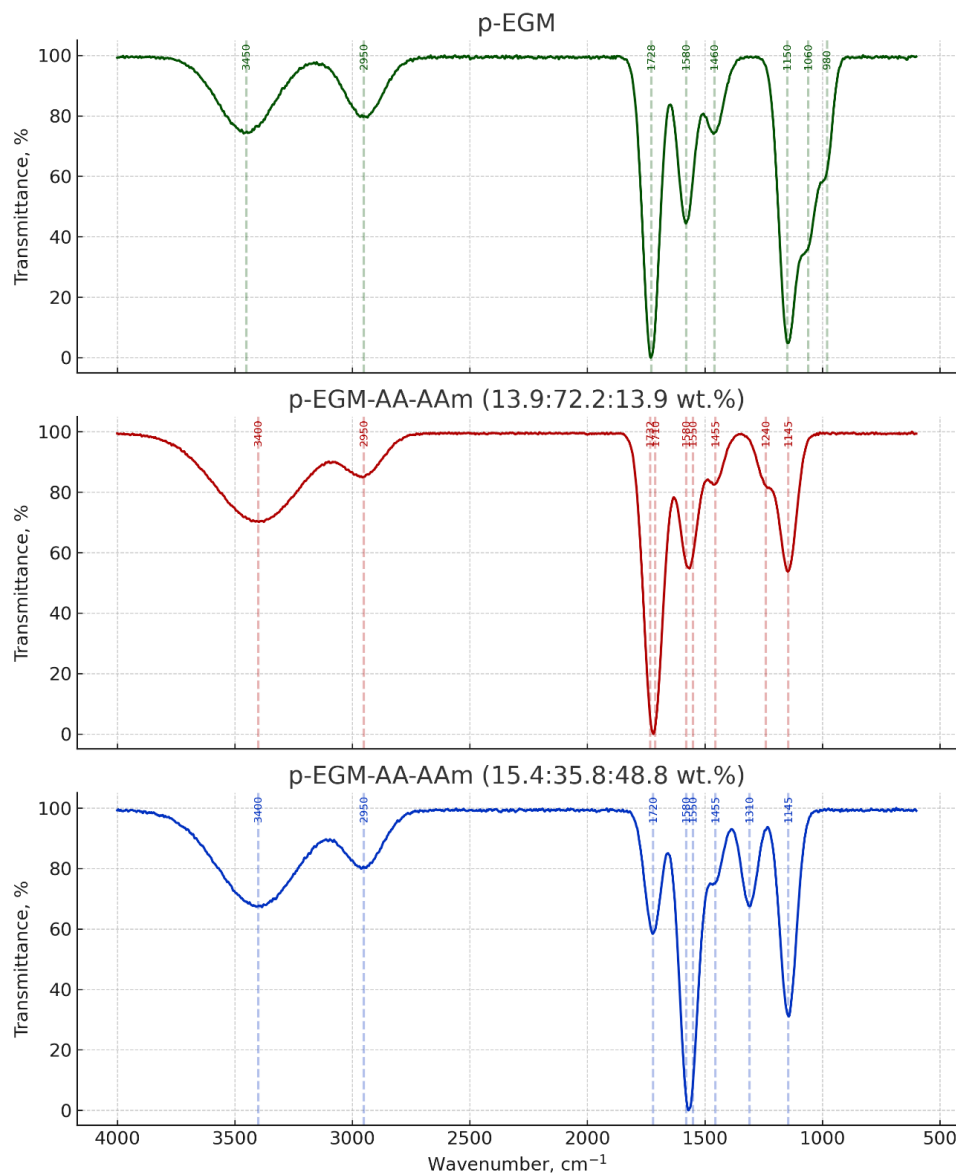


Figure 2. IR spectra of the initial p-EGM and p-EGM-AA-AAm terpolymers

The IR spectra of the initial p-EGM and p-EGM-AA-AAm terpolymers of various compositions show a characteristic set of bands confirming the formation of the corresponding structures. Thus, for the initial p-EGM, an intense band of valence vibrations of the carbonyl group of ester fragments is observed at 1725–1730 cm^{-1} , as well as a characteristic peak of unsaturated $\text{C}=\text{C}$ bonds of maleate units in the range of 1575–1590 cm^{-1} . The bands of CH_2 deformation vibrations appear in the range 1455–1465 cm^{-1} , while the intense bands in the region 1140–1160 cm^{-1} correspond to the vibrations of the $\text{C}-\text{O}-\text{C}$ polyester chain.

When containing a significant amount of AA (terpolymer p-EGM-AA-AAm with a composition of 13.9:72.2:13.9 wt.%), a broad absorption band appears in the spectrum in the 3100–3600 cm^{-1} region, caused by the superposition of the bands of the –OH carboxyl groups and hydrogen-bonded fragments. An important feature is the strengthening of the carboxyl vibration band –COOH at 1710–1715 cm^{-1} , the intensity of which exceeds that of the initial p-EGM and indicates an increase in the proportion of acrylic acid in the structure. The band of unsaturated double bonds at 1575–1585 cm^{-1} is preserved but noticeably decreases in intensity, which is characteristic of the partial conversion of –C=C bonds during terpolymerization.

In the terpolymer with a higher AAm content (p-EGM-AA-AAm composition 15.4:35.8:48.8 wt.%), further redistribution of band intensities is observed. A pronounced amide band appears in the spectrum at 1550–1555 cm^{-1} , as well as a band of amide vibrations in the region of 1305–1315 cm^{-1} . These bands become dominant, which is consistent with an increase in the proportion of amide fragments. Broad absorption in the 3200–3400 cm^{-1} region indicates the contribution of –NH amide groups, which form stable hydrogen bonds in the polymer structure. The –C=O band of ester groups shifts to 1720–1725 cm^{-1} and decreases slightly in intensity due to the dilution of polyester links with acrylamide (Figure 2).

Thus, a significant decrease in the intensity of the bands corresponding to the vibrations of unsaturated double –C=C bonds indicated a high degree of radical terpolymerization. The spectra showed characteristic bands of carboxyl, amide, and ether groups, confirming the presence of all functional fragments involved in the formation of a three-dimensional network. In samples with an increased AA content, an intensification of the carboxyl bands was observed, which corresponded to an increased number of ionogenic centres and a more pronounced polyelectrolyte character of the polymer network.

Further, by analyzing the cured samples based on p-EGM with AA and AAm, their densities and volume shrinkage index were determined, which for gel materials should not exceed 15 %.

The density of the cured products was measured by the hydrostatic method. Based on the results of the densities of the initial solutions and cured samples, the total volume shrinkage was calculated [21]. The results are presented in Table 3.

Table 3

Dependence of terpolymers properties on mass composition of p-EGM-AA-AAm, PB + DMA (1 % + 0.15 %), $T = 293 \text{ K}$

Composition of initial mixture, wt.%			Density of the dried sample (ρ_d), g/cm^3	Volume shrinkage, %	Density of the swollen sample (ρ_s), g/cm^3
p-EGM	AA	AAm			
13.9	72.2	13.9	0.9128±0.0456	13.5	1.0254±0.0513
14.1	52.5	33.4	0.9512±0.0476	11.8	1.0361±0.0518
15.4	35.8	48.8	0.9841±0.0492	10.5	1.0408±0.0520

Based on the results obtained, it can be concluded that the density of the cured samples decreased relative to the initial solutions, which reflected the formation of internal porous volume. It should be noted that samples with an increased AA content were characterized by lower density ($\rho_d = 0.9841 \text{ g/cm}^3$), which reflected the formation of a more sparse polymer network with increased internal volume and a higher degree of hydration. Table 3 also shows the densities of the synthesized gel samples after 24 hours of immersion in water. Considering that with an increase in the AAm content, the polymer fraction in the swollen gel volume is higher, this contributes to an increase in the density value of the studied sample p-EGM-AA-AAm with a composition of 15.4:35.8:48.8 wt.%.

Next, in order to establish the influence of external factors on the behavior of the studied hydrogels, studies were conducted on the effect of pH and temperature on them. When evaluating the prospects for the use of polymer gels as a basis for gel bandages and plasters, it is necessary to take into account conditions that are as close as possible to physiological ones. Thus, human skin and subcutaneous tissues are characterized by a slightly acidic surface reaction (pH 4.5–5.5) due to the lipid barrier and the presence of weak organic acids. When the skin is damaged, the pH shifts to neutral and slightly alkaline values (pH 6.0–8.0) due to the release of interstitial fluid and exudate containing proteins and salts.

The pH range of 4–8 covers all typical conditions of contact between the material and the skin and wound surface — from healthy epidermis to inflamed or infected tissues. More acidic (pH < 4) and more alkaline (pH > 8.5) conditions do not occur in physiological practice and can cause protein denaturation and destruction of the skin's barrier function, so they were not considered in this study.

The study of the degree of swelling of 0.5 g gel samples (Figure 3) in the pH range of 4–8 revealed a significant sensitivity of the structure to the acidity of the environment. When the pH was reduced to 4.0–5.5, gel compression (collapse) was observed, accompanied by a decrease in its volume and moisture content. This is due to the protonation of carboxyl groups, which reduces the charge repulsion between polymer chains and causes the network to compact [17]. This behavior is consistent with the acid–base properties of acrylic acid ($pK_a \approx 4.25$), which governs the degree of ionization of the carboxyl groups within the studied pH range. At pH values below the pK_a , the $-\text{COOH}$ groups remain predominantly protonated, resulting in reduced electrostatic repulsion and contraction of the polymer network. Conversely, at pH values above the pK_a , progressive dissociation of the carboxyl groups occurs, leading to increased charge density and enhanced swelling of the hydrogel. This behavior may be advantageous for potential wound dressing applications, since in the acidic environment of healthy skin, the material retains its shape, does not over-moisten the surface and provides a barrier function.

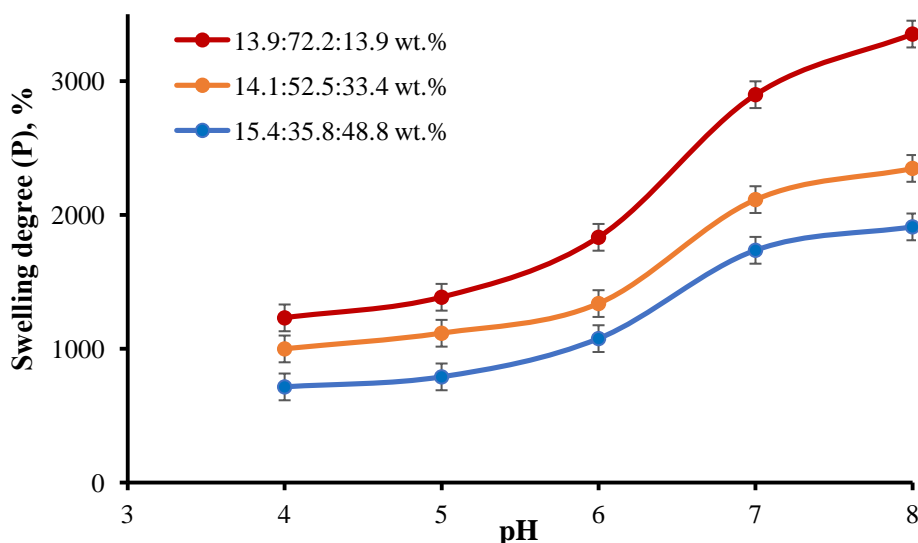


Figure 3. The influence of pH on the swelling of p-EGM–AA–AAm terpolymers

In the acidic range (pH 5–6), the carboxyl groups remained predominantly undissociated, the network remained compact, the internal porosity was minimal, and the degree of swelling was low. When the pH was increased to neutral and slightly alkaline values (pH 7–8), the carboxyl groups dissociated and negative charges accumulated, causing electrostatic repulsion between the macromolecules within the network. This led to its expansion and increase in volume, tending to minimize the free energy of the system, and, accordingly, to an increase in the sorption capacity of the material. For the samples analyzed, the degree of swelling at pH 8.0 reached its maximum value. This effect can be useful when the dressing comes into contact with wound exudate, which usually has a slightly alkaline reaction: in this case, the gel will actively absorb excess moisture, preventing tissue maceration.

It is also worth noting that the strongest increase in the degree of swelling was recorded in samples with a high AA content, where the proportion of ionogenic groups was significant. At the same time, analysing the dynamics of swelling of the analyzed gels, it is possible to conclude that water sorption is a two-stage process. Thus, in the first stage, large pores are quickly filled. The second stage consists of a slower rearrangement of the dense segments of the network. It is worth noting that in samples with a high AA content, the process of reaching equilibrium was faster, which indicated high structural fluctuation mobility. A slight acidification of the solution (pH ~6) was also observed during prolonged exposure of samples with a high AA content, caused by the release of some undissociated carboxyl groups.

Further investigation of the effect of temperature (35–39 °C) on the synthesized gels revealed a pronounced thermosensitive response, manifested in the form of a sharp, abrupt collapse (Figure 4). In particular, when the temperature was raised to ~37–38 °C, a partial collapse of the gel structure was observed, accompanied by intense water release from the polymer network. This effect is associated with a disturbance in the equilibrium between hydrophilic interactions and the internal cohesive forces of the polymer chains:

when heated, some of the hydrogen bonds are broken, the thickness of the hydrate shell decreases, which leads to a decrease in the volume of the gel and an increase in the proportion of hydrophobic interactions.

After the temperature was lowered, the structure of the gels was partially restored, but there was no complete return to the initial state. This is explained by the relaxation of the chains and partial fixation of new configurations during heating, as well as the possible redistribution of interchain bonds. The observed temperature memory effect indicates a shallow but significant redistribution of cross-link density in local areas of the gel.

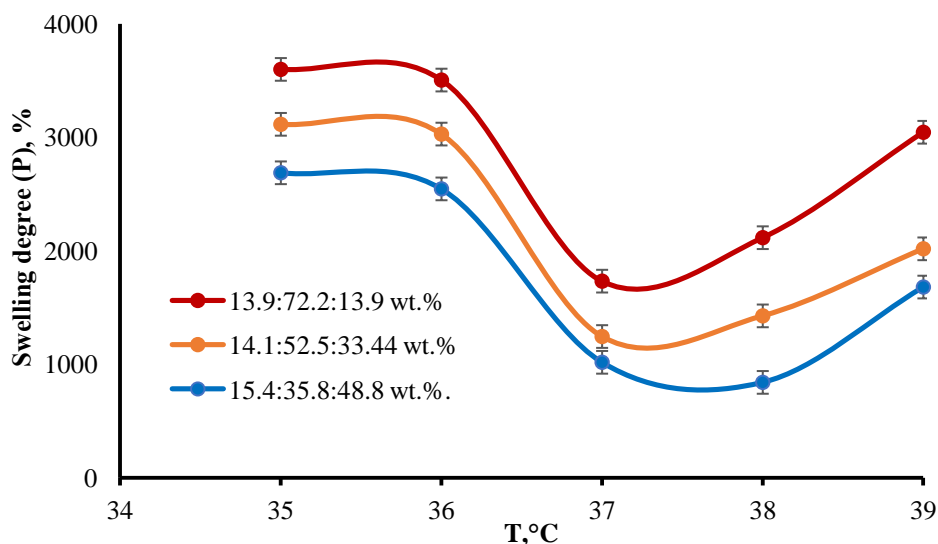


Figure 4. The influence of temperature on the swelling of p-EGM-AA-AAm terpolymers

Thus, gels with a high AA content (Figure 4) demonstrated a particularly strong thermal response. This is due to their polyelectrolyte nature: when heated, the degree of ionization of carboxyl groups decreases, reducing the electrostatic repulsion between polar fragments, which contributes to collapse. In addition, large hydrate shells around -COOH fragments are more sensitive to temperature changes, which increases the rate of dehydration and leads to a more pronounced change in volume.

An additional factor that enhances thermosensitivity is the difference in the mechanical flexibility of reactive segments: more mobile chains in gels with a high AA content are more easily rearranged under the influence of temperature, which leads to a more pronounced volume transition. At the same time, systems with a high AAm content retain residual hydration when heated due to the presence of amide groups, which makes their thermal response less pronounced [6, 14]. Thus, the thermosensitivity of the gels under study is the result of a complex combination of hydration, ionic interactions, chain configurational mobility, and local crosslink density. These features are particularly important for the use of materials as gel dressings and thermosensitive delivery systems: controlled moisture release upon heating helps maintain optimal wound surface hydration, and partial volume transition can promote prolonged drug release.

Subsequently, scanning electron microscopy (SEM) examination (Figure 5) of the structure of the synthesized hydrogels revealed significant differences in the morphology of the samples depending on their composition. An increase in AA content (Figure 5a) contributed to the formation of a looser, porous structure with well-defined channels and local cavities of various sizes. This structure is characterized by increased pore space openness, which facilitated water penetration and accelerated the swelling process. The presence of partially branched pore clusters also indicates less dense packing of chains during the formation of the polymer network. In contrast, the gel with an increased AAm content of ~ 50 wt.% (Figure 5b) is characterized by a more compact structure with fewer large pores. The SEM image of this sample (Figure 5b) shows small, isolated pores without a pronounced channel system, and the structure itself appears denser. This indicates a tighter packing of macromolecules and a higher local cross-link density, which limits the inflow and retention of water in the material volume and leads to a decrease in the degree of swelling.

The morphological data obtained are consistent with the results of studies of sorption characteristics: loose structures with a large number of macro- and mesopores demonstrated higher water absorption capacity, while compact structures with a predominance of micropores provided limited swelling. Thus, the identi-

fied relationship between the chemical composition of terpolymers and the structure of the three-dimensional polymer network allows for targeted regulation of the morphology, porosity, and functional properties of hydrogels by varying the ratio of AA and AAm.

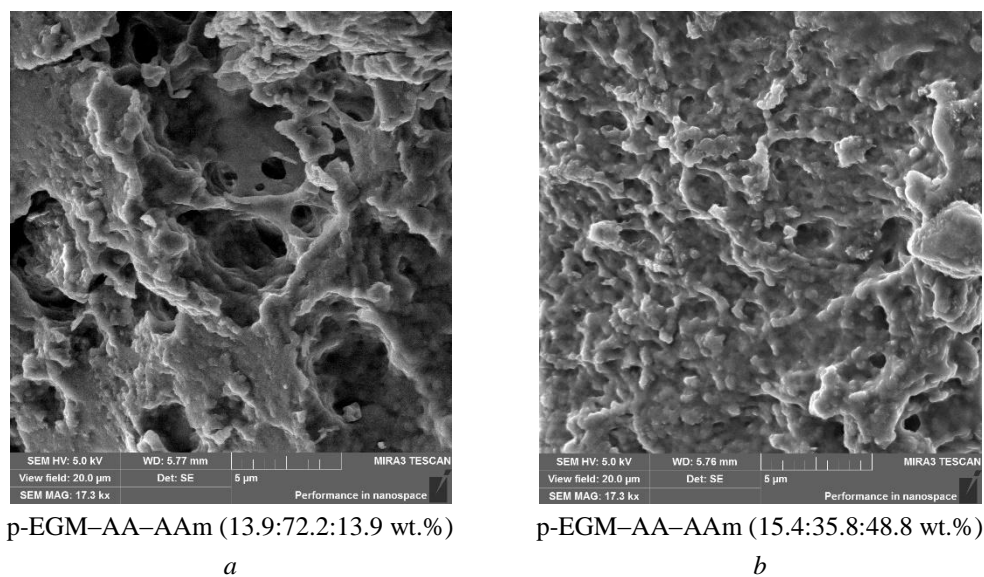


Figure 5. SEM-images of the p-EGM-AA-AAm terpolymers

It is worth noting that the observed differences may be related to the peculiarities of the terpolymerization mechanism. Thus, AA, with its strong hydrophilicity and ionization ability, contributes to the formation of a more sparse three-dimensional network, while AAm, on the contrary, forms smoother and more densely packed structures due to amide groups capable of multiple interchain interactions. These results highlight the key role of monomer composition in the formation of the final morphology and allow us to predict the operational properties of the resulting gels in real-world conditions [14].

Furthermore, TG analysis data showed that the thermal decomposition of the studied hydrogels proceeds in two main stages. The first stage corresponds to the removal of weakly bound and partially adsorbed water. In this section (Figure 6), samples with a higher AA content showed a more pronounced peak in mass loss, which is associated with the increased hydrating ability of the polyelectrolyte network and the large number of ionogenic groups that retain water.

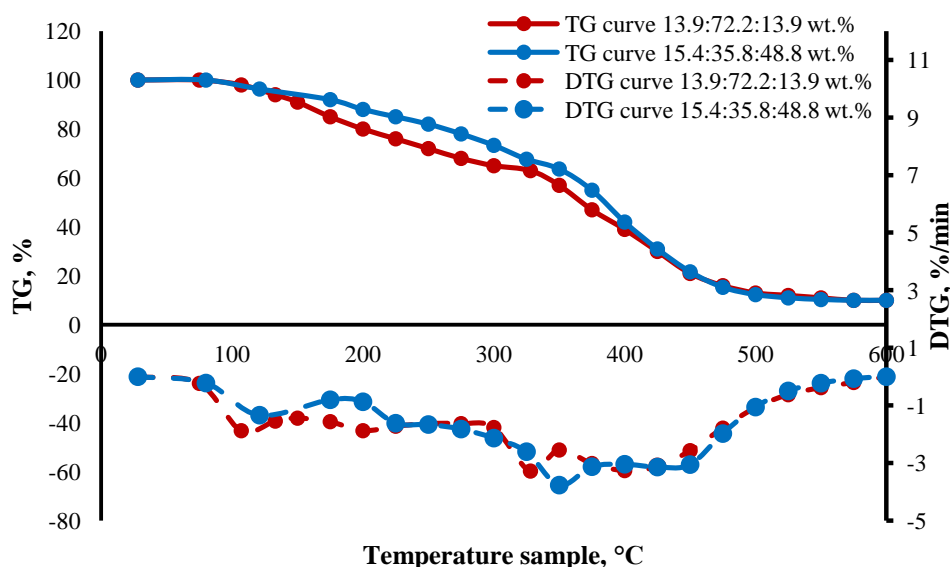


Figure 6. TG-analysis of the p-EGM-AA-AAm terpolymers

The decomposition onset temperature depended significantly on the chemical composition of the terpolymers. For the p-EGM-AA-AAm composition of 13.9:72.2:13.9 wt.%, decomposition began at ~107 °C, while the sample with a composition of 15.4:35.8:48.8 wt.% showed a higher heat distortion temperature of ~121 °C. This behavior may be attributed to differences in intermolecular interactions and network organization associated with the monomer composition.

The second stage, corresponding to the destruction of the organic polymer backbone, was also characterized by a shift in the maximum decomposition temperature. For the p-EGM-AA-AAm terpolymer with a composition of 13.9:72.2:13.9 wt.%, the maximum decomposition occurred at ~328 °C, while for the composition with a ratio of 15.4:35.8:48.8 wt.%, it shifted to a higher temperature range of ~348 °C, confirming the more thermally stable and rigid structure of the polymer with an increase in AAam content.

Complete carbonization of the samples was completed at ~585–590 °C, after which the remaining inorganic residue was about 7 % for the system with a composition of 13.9:72.2:13.9 wt.% and about 9 % for the p-EGM-AA-AAm terpolymer with a composition of 15.4:35.8:48.8 wt.%. The increase in residue also reflects a denser spatial network and a higher degree of structural organization of samples with increased AAam content.

Conclusions

The physicochemical properties of p-EGM-AA-AAm terpolymer hydrogels obtained by “cold” curing were systematically investigated. It was established that increasing the acrylic acid content promotes the formation of polyelectrolyte-type networks characterized by a high swelling degree (up to 2898 %), developed porosity, and pronounced sensitivity to external stimuli.

At the same time, acrylamide was shown to act primarily as a structure-forming non-ionogenic component that enhances network compactness and thermal stability through hydrogen-bond interactions. The synthesized materials exhibited controlled volumetric shrinkage not exceeding 10.5–13.5 %, indicating the formation of structurally stable three-dimensional networks.

The hydrogels demonstrated clear responsiveness in the physiologically relevant pH range of 4–8 and at temperatures of 35–39 °C, confirming their adaptive behavior under conditions close to biological environments. Among the studied compositions, the p-EGM-AA-AAm system with a ratio of ~15:70:15 wt.% showed the most balanced combination of swelling capacity, structural integrity, and porous morphology.

Overall, the obtained results indicate that the developed hydrogels may be considered promising candidates for potential use in sorption-active polymer matrices and hydrogel-based wound dressing systems.

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Conflicts of Interest

The authors declare no conflict of interest.

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