Hydrogels based on poly(2-hydroxyethyl methacrylate) and nettle extract*)

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Abstract: New types of hydrogels based on linear poly(2-hydroxyethyl methacrylate) and poly(ethylene glycol) diacrylate (PHEMA-PEGDA) and nettle extract were obtained. A solution of poly(2-hydroxyethyl methacrylate) in monomer (S-PHEMA) was obtained by bulk photopolymerization. Common nettle extract was used as an ingredient that facilitates wound healing. The influence of the photoinitiator content (1-[4-(2-hydroxymethyl)-phenyl]-2-hydroxy-2-methylpropanone) on the photopolymerization kinetics, as well as the equilibrium swelling ratio (ESR), thermal and mechanical properties of the hydrogels were examined. Complete HEMA conversion was achieved at the lowest photoinitiator dose. Replacing HEMA with S-PHEMA causes an increase in ESR (24%) and T_g (50°C) and the amorphous phase content. At the same time, the tensile strength and Young's modulus decrease. However, the addition of nettle extract (0.3 wt%) requires a significant increase in the amount of photoinitiator (up to 2.5 wt%). As the concentration of the photoinitiator in the system increases, ESR and T_g decrease, but tensile strength and Young's modulus increase.

Keywords: hydrogels, photopolymerization, HEMA, nettle extract.

Hydrożele na bazie poli(metakrylanu 2-hydroksyetylu) i ekstraktu z pokrzywy

Streszczenie: Otrzymano nowego typu hydrożele na bazie liniowego poli(metakrylanu 2-hydroksyetylu) i diakrylanu poli(glikolu etylenowego) (PHEMA-PEGDA) oraz ekstraktu z pokrzywy. Roztwór poli(metakrylanu 2-hydroksyetylu) w monomerze (S-PHEMA) otrzymano w procesie fotopolimeryzacji w masie. Ekstrakt z pokrzywy zwyczajnej użyto jako składnik ułatwiający gojenie się ran. Zbadano wpływ zawartości fotoinicjatora (1-[4-(2-hydroksymetylo)-fenylo]-2-hydroksy-2-metylopropanonu) na kinetykę procesu fotopolimeryzacji, a także na równowagowy współczynnik pęcznienia (ESR), właściwości termiczne i mechaniczne hydrożeli. Całkowitą konwersję HEMA uzyskano przy najniższej dawce fotoinicjatora. Zastąpienie HEMA przez S-PHEMA powoduje wzrost ESR (24%) i T_g (50°C) oraz udziału fazy amorficznej. Jednocześnie zmniejsza się wytrzymałość na rozciąganie i moduł Younga. Natomiast dodatek ekstraktu z pokrzywy (0,3 cz. mas.) wymaga znacznego zwiększenia ilości fotoinicjatora (do 2,5 cz. mas.). Wraz ze wzrostem stężenia fotoinicjatora w układzie maleje ESR i $T_{g'}$ ale wzrasta wytrzymałość na rozciąganie i moduł Younga.

Słowa kluczowe: hydrożele, fotopolimeryzacja, HEMA, ekstrakt z pokrzywy.

Hydrogels are three-dimensional, hydrophilic, polymeric networks capable of absorbing large amounts of water or biological fluids in a reversible manner [1]. Due to their high-water content, porosity, and soft consistency, they closely imitate natural living tissue, more than any other class of synthetic biomaterials [2, 3]. Hydrogels are available on the market in solid or liquid forms [4], thanks to which, they are commonly used in practice clinical and experimental medicine in a wide range, from controlled drug delivery systems, tissue engineering and regenerative medicine, to diagnostics, cell immobilization, separation of biomolecules or cells, or are used as barriers regulating biological adhesion [5]. One of the most common methods of obtaining hydrogels is photopolymerization. Photo-crosslinkable hydrogels, including 2-hydroxyethyl methacrylate (HEMA)

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or poly(ethylene glycol)diacrylate (PEGDA) have been extensively explored in biomedical fields due to outstanding properties, such as biocompatibility, hydrophilicity and biodegradability [6]. The first hydrogel materials were derived from HEMA [7]. To this day, HEMA and PEGDA are one of the most frequently used monomers for the synthesis of hydrogels and are often modified. For example, PEGDA with natural polysaccharides such as gelatin, alginate, and chitosan can be synergized to increase its control over biocompatibility [8-11]. A method of obtaining hydrogels from low molecular weight PEGDA prepolymers by photopolymerization is also known [12]. Dumitrescu *et al*. revealed novel casein-based hybrids embedded in a PHEMA-PEGDA hydrogel for potential use in bone repair and regeneration [13]. Hydrogels based on HEMA and PEGDA are also appealing as scaffolds for tissue reconstruction, being biocompatible and hydrophilic [14, 15]. The PHEMA-PEGDA scaffolds are easy to produce, non-toxic, and mechanically stable enough to resist fracturing during routine handling. However, for achieving such parameters, the polymerization conditions and the molar ratios of these reagents are crucial [16]. It was alleged that PEGDA is more hydrophilic than PHEMA, thus only small volumes of PEGDA may be used to preserve phase separation in the copolymer and crosslink HEMA. Greater hydrophilicity introduced by PEGDA can suppress phase separation by increasing the solubility of the copolymer chains [17]. Other researchers confirm that the addition of HEMA to PEGDA-based hydrogels are helpful in improving the swelling properties, because the HEMA can provide more hydroxyl group and strong H-bonding interactions between the hydrogels and water [18]. It was shown that the equilibrium water content of PEGDA and HEMA-based hydrogels was strongly affected by the HEMA content. Systems with higher HEMA concentration (40 wt% HEMA: 60 wt% PEGDA) showed a more hydrophilic surface than those with lower HEMA content (10:90) [18]. Nevertheless, HEMA-based hydrogels have stronger mechanical properties than others [19]. So poly(ethylene glycol) diacrylate of different molecular weights was often used as crosslinking agent for the photopolymerization of HEMA in order to obtain HEMA/PEGDA-based hydrogels. Thermal studies have shown that the increase PEGDA molecular weight increases glass transition temperature and thermal stability of such systems [20]. Despite many years of research, possible applications of hydrogels in fields related to human health and medicine cause that these materials are still in the center of attention of scientists. The incorporation of

synthetic medicinal substances (e.g., doxorubicin [21, 22], amoxicillin, and other antibiotics [23] and antimicrobial substances [24]) or natural substances (honey [25], herbal extracts [26], *Eupatorium glutinosum* [27], aloe vera [28, 29], and other plant extracts) into the structure of the hydrogel matrix are widely described. Also known are hydrogels containing rosemary extracts or marigold flowers (*Calendula*) [30]. Histopathological results are showing, that a hydrogel containing a 7 wt% of *Calendula* extract was effective in healing skin wounds [31]. Stinging nettle (*Urtica dioica*) commonly known for its health properties, because is rich in minerals, including (calcium, magnesium, phosphorus, copper, iron, potassium, and zinc) and vitamins (vitamin A, vitamin C, thiamine, riboflavin and vitamins C, D, E and K) [32]. In addition, the leaves of this plant contain fatty acids, polyphenols (ferulic acid, gallic acid, syringic acid), flavonoids (catechin hydrate) and other chemical compounds [33, 34]. Studies have shown, that nettle extracts, due to the content of carotenoids, have anti-aging, anti-inflammatory and anti-cancer properties [35]. Bouassida *et al*. in 2017 showed that nettle extract increases the rate of wound healing by up to 30%. Histopathological evaluation confirmed that within eleven days nettle extract significantly closed the wound and caused complete regeneration of the epidermis [36].

This paper describes the properties of new PHEMA-PEGDA hydrogels containing nettle extract, as potential wound-healing dressings. The innovation of this solution consists of replacing the HEMA monomer with HEMA polymer solution (S-PHEMA) containing approx. 50 wt% of linear homopolymer. Such solution can be obtained in easy and environmentally friendly way by bulk photopolymerization process. This allows for increase in the proportion of water and reduction of concentration of the photoinitiator in hydrogel formulation process. The influence of photoinitiator concentration on the process of cross-linking photopolymerization of HEMA prepolymer with PEGDA cross-linking agent and nettle extract as well as the thermal and mechanical properties of the obtained hydrogels were investigated.

EXPERIMENTAL PART

Materials

The following components were used for the preparation of the hydrogels: 2-hydroxyethyl methacrylate (HEMA; 97% containing < 250 ppm of monomethyl ether
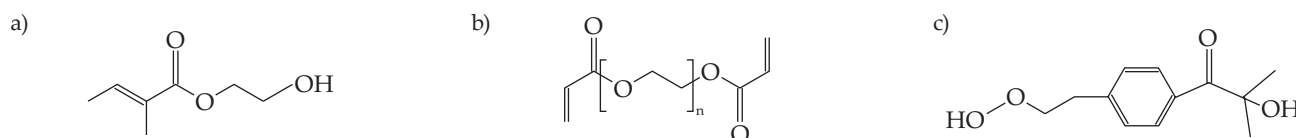

Fig. 1. Chemical structures of the reagents: a) 2-hydroxyethyl methacrylate, b) poly(ethylene glycol) diacrylate, c) photoinitiator Omnirad 2959

T a b l e 1. Composition of hydrogels

Hydrogel	Components					
	Distilled water, wt%	HEMA wt%	S-PHEMA wt%	PEGDA 700[a]	O2959[b]	Nettle extract[a]
H025	75	25	–	2.4	1	–
HS25		–	25		0.85	
HS20	80	–	20			
HS20N/0.85	80	–	20	2.4	0.85	0.3
HS20N/1.5					1.5	
HS20N/2.5					2.5	

a – wt%/ 100 wt% of HEMA (or S-PHEMA) and distilled water, b – wt%/100 wt% mixture containing HEMA (or S-PHEMA), and PEGDA 700

hydroquinone as inhibitor; Sigma-Aldrich, St. Louis, MO, USA), poly(ethylene glycol) diacrylate (PEGDA700; Mn= 700 g/mol; Sigma-Aldrich, St. Louis, MO, USA), 1-[4-(2-hydroxyethoxyl)-phenyl]-2-hydroxy-2-methyl-propanone (Omnirad 2959; IGM Resins, Waalwijk, The Netherlands), distilled water and nettle extract (NE; pure nettle leaf extract; contains 1 g of silica and 2.2 g of polyphenols in 100 g of extract; Soul Farma, Bielsko-Biała, Poland).

All the reactants were used without purification. The chemical structures of the reagents are shown in Figure 1.

Methods

Synthesis and characterization of poly(2-hydroxyethyl methacrylate) solution

The UV-homopolymerization process of HEMA was carried out in the presence of the inert gas (argon) at room temperature for 10 min in a glass reactor (250 ml) equipped with a mechanical stirrer, thermocouple, and a cooler. The high-intensity UV lamp (UVAHAND 250, Dr. Hönle AG UV Technology, Gräfelting, Germany) was placed perpendicularly to the side wall of the reactor as a UV radiation source. The UV-irradiation inside the reactor (15 mW/cm^2) was controlled using the SL2W UV-radiometer (UV-Design, Germany). Temperature changes in the reactor were monitored in real time. The dynamic viscosity of S-PHEMA i.e., solution of homopolymer HEMA in unreacted HEMA monomer, was measured at 25°C using the DV-II Pro Extra viscometer (spindle #6, 50 rpm; Brookfield, New York, NY, USA). Solids content of S-PHEMA was determined using the thermobalance (Radwag, Poland); S-PHEMA sample (ca. 2 g) was heated in an aluminum pan at 105°C for 4 h. Moreover, the kinetics studies of the UV-homopolymerization process were performed at 25°C by the photo-DSC method (the differential scanning calorimeter with UV equipment; Q100, TA Instruments, New Castle, DE, USA). During the measurements, samples (5 mg) were UV-irradiated (320–390 nm) with an intensity of 15 mW/cm^2 in argon

atmosphere. Polymerization rate (R_p, s^{-1}) was calculated according to Equation (1) and conversion of double bonds (p, %)—according to Equation (2) [37].

$$R_p = \frac{\left(\frac{dH}{H_0}\right)}{H_0} \qquad (1)$$

$$p = \frac{\Delta H_t}{\Delta H_0} \cdot 100 \ [\%] \qquad (2)$$

where: dH/dt – the recorded heat flow during UV-irradiation, H_0 – the theoretical heat value for the complete degree of conversion (54.8 kJ/mol for methacrylate) and ΔH_t – the reaction heat evolved at t-time.

Hydrogel preparation

Preparation of hydrogels was carried out in polystyrene pans with a diameter of 11 cm; where the mixtures of components consisting of HEMA or PHEMA solution (S-PHEMA), the crosslinking monomer PEGDA700, the photoinitiator O2959, nettle extract and distilled water were placed. Reaction mixtures were continuously purged with nitrogen gas to displace the air of the system avoiding inhibition of the photopolymerization process. The mixtures were irradiated at UV-A range with UV-A lamp (UVAHAND 250, Dr. Hönle AG UV Technology, Gräfelting, Germany) for 30 min. UV-dose was 5 mW/cm^2. The UV-irradiation was controlled using the SL2W UV-radiometer (UV-Design, Brachttal, Germany). The mixture compositions of the hydrogel systems are shown in Table 1.

Three types of hydrogels were obtained. The first (reference samples, H025) was a hydrogel based on HEMA monomer and PEGDA700 cross-linking monomer (Figure 2a). The second type of hydrogels were those that use preprepared PHEMA solutions containing poly(2-hydroxyethyl methacrylate), i.e., S-PHEMA. The preparation of S-PHEMA is shown in Figure 2b. The third hydrogel type based on S-PHEMA solution and contains nettle extract. Their preparation is shown in Figure 2c.
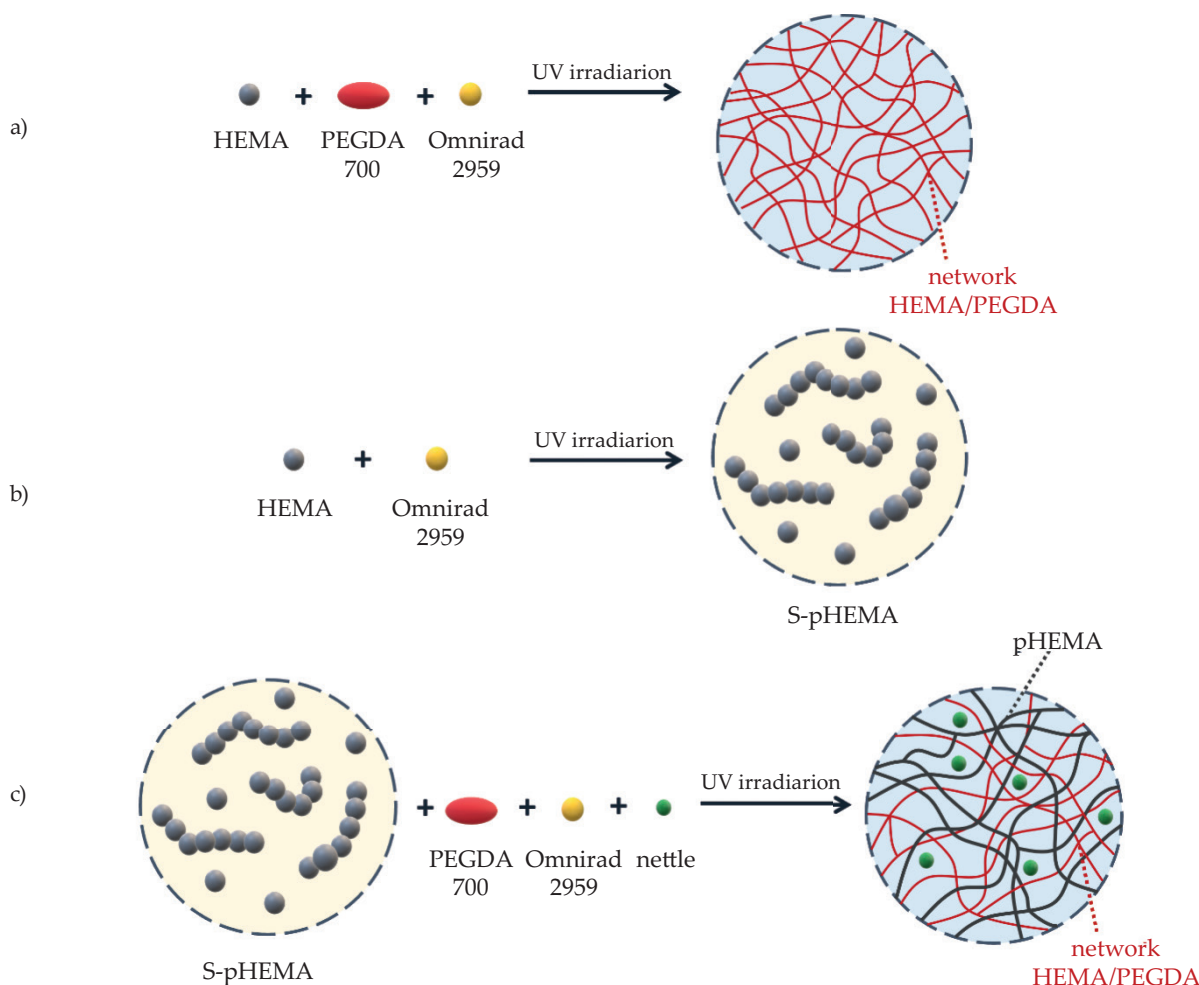
Fig. 2. The scheme of hydrogels preparation

Characterization of hydrogels

The morphology of the hydrogels (i.e., the appearance of the samples, their flexibility or cross-linking) was assessed visually.

The structure of hydrogels was monitored using the Fourier transform infrared spectroscope with ATR accessories (Nicolet 380, ThermoScientific, Waltham, MA, USA). Before testing, the hydrogel samples were dried at 37°C for 48 h. The absorbance of the characteristic bands, i.e., 812 cm^{-1} assigned to the C=C stretching vibrations in HEMA [38], and 1635 cm^{-1} assigned to C=C in [39] PEDGA was checked. The swelling ratio of the prepared hydrogels was carried out by determining the equilibrium swelling ratio (ESR). The hydrogel samples (ca. 1 g, dried before the test at 37°C for 48 h) were immersed in distilled water for 1 h at 37°C. Excess water was removed from surface of hydrogel. The ESR was calculated by Equation (3):

$$ESR = \frac{w_e - w_d}{w_e} \cdot 100\% \qquad (3)$$

where w_d and w_e represent weight of the dry gel and swelled gel, respectively [40].

To examine the thermal properties of the prepared hydrogel modulated differential scanning calorimetry (MDSC) analyses were carried out using differential scanning calorimeter DSC 250 (TA Instruments, New Castle, DE, USA). The measurements were carried out at temperature range between –80 and 250°C. The heat flow rates were recorded at a rate of 3°C per minute under nitrogen atmosphere. Glass transition temperatures (T_g) of hydrogels and parameters characteristic for crystallization processes were determined.

The mechanical properties of hydrogel systems, i.e., tensile strength and Young's modulus were analyzed using universal testing machine (Instron 5982, Instron, Norwood, MA, USA) at room temperature, according to the ISO 527-2 type 5A [41]. Before the test hydrogels samples were dried at 37°C for 24h. Each measurement was repeated three times, and the final values were given as the average value.

RESULTS AND DISCUSSION

Kinetics of the UV-homopolymerization of HEMA

The aim of the research was to improve the swelling ratio, and mechanical properties of HEMA and PEGDA-based hydrogels by replacing the HEMA monomer with
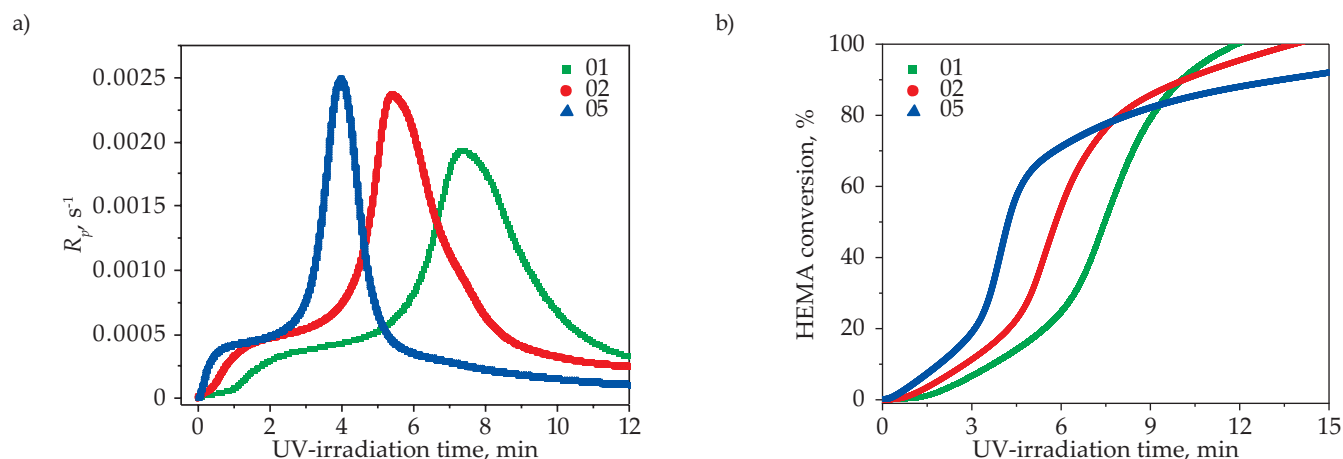
a)

b)

Fig. 3. Reaction rate (a) and conversion of double bonds (b) depending on UV exposure time and photoinitiator dose

a solution of its homopolymer, i.e., S-PHEMA. To obtain such a solution, the process of HEMA homopolymerization in bulk was initiated by UV radiation. The process was carried out in a glass reactor, and the monomer and photoinitiator were mechanically stirred during the reaction (300 rpm). Selection of the photoinitiator dose for the process was carried out based on the analysis of photo-DSC results. The kinetics of UV-initiated homopolymerization of HEMA monomer was investigated. The reaction rate (R_p) and the conversion of double bonds (p), in this case identical to the conversion of the HEMA monomer, depending on UV-irradiation time and photoinitiator dose are presented in Figure 3.

It is known that the rate of photopolymerization generally increases with the amount of photoinitiator used. It is worth noting, that the maximum reaction rate appears very late, compared to classically studied photopolymerization systems. At the highest dose of photoinitiator, the system reached $R_p^{\max}$ after 4 min of UV-irradiation. At the lowest dose of photoinitiator, $R_p^{\max}$ is reached after nearly 8 minutes. At the beginning, the rate of HEMA photopolymerization increases rapidly over a short period of time until it reaches a steady state. This effect is mildest at low concentration of photoinitiator, although steady state is still noticeable. Further, the reaction proceeds in a steady state, and the rate of photopolymerization practically does not increase as a result of the decrease in monomer concentration at a constant concentration of radicals. At a certain degree of conversion, a gel effect appears and the rate of photopolymerization rapidly increases until reaching the maximum possible value of $R_p^{\max}$. The reaction then proceeds at a steadily decreasing rate until the monomer is completely consumed. The gel effect (p_g) and the monomer conversion in reaching $R_p^{\max}$ are shown in Figure 4. As can be seen, the gel effect, practically independent of the concentration of the photoinitiator, is achieved at approx. 10% HEMA conversion. For example, it has been found that during the photopolymerization of methyl methacrylate, the gel effect will occur at about 20–25% conversion [38]. In the case of the HEMA monomer, we find that the gel effect occurs

much earlier. This is related to the presence of a hydroxyl group, which is confirmed by our previous research on the influence of the monomer structure on the bulk photopolymerization process [42]. As can be seen, a higher dose of photoinitiator causes generally rapid photopolymerization. In cases of 0.5 wt. part of O2959 in the time interval between 3 and 5 minutes of UV exposure, there is a rapid increase in monomer conversion, up to 70%. However, the total monomer conversion after 15 min of irradiation is ca. 90% and is lower than with a lower addition of photoinitiator. Complete monomer conversion (100%) after 12 minute of UV-irradiation was achieved for the system with 0.1 wt% of photoinitiator. The curve of conversion versus exposure time (Fig. 3b) was smoother. For these reasons, it was decided that the bulk HEMA photopolymerization process should preferably be carried out at a low concentration of photoinitiator, i.e., 0.1 wt%.

The physicochemical properties of PHEMA solution

The course of the UV-photopolymerization process in the glass reactor was investigated by the recording the temperature of the mixture as illustrated in Fig. 5 for the system with 0.1 wt% of O2959.

As can be seen, there is no clear maximum temperature in the HEMA photopolymerization thermogram. During photo-DSC tests, the system with 0.1 wt% of photoinitiator after just 8 minutes maximum reaction rate was recorded. Our previous studies indicate that the bulk photopolymerization process differs from thin film photopolymerization because the mechanical mixing of the reactants during exposure increases the time to reach the reaction temperature peak (maximum reaction rate). UV-homopolymerization of HEMA was completed after only 10 minutes because the extension of the reaction time led to a sudden and rapid increase in temperature and gelation of the system. The obtained product i.e., a solution of HEMA homopolymer in unreacted monomer (S-PHEMA), was characterized by a viscosity of 4 Pa·s and a solids content of 50.4%.

Hydrogels characterization

Based on the visual evaluation of the prepared hydrogels (Table 2), it was found that all samples were cross-linked after 30 minutes of UV-irradiation in argon atmosphere. The surfaces of the hydrogels were moist but did
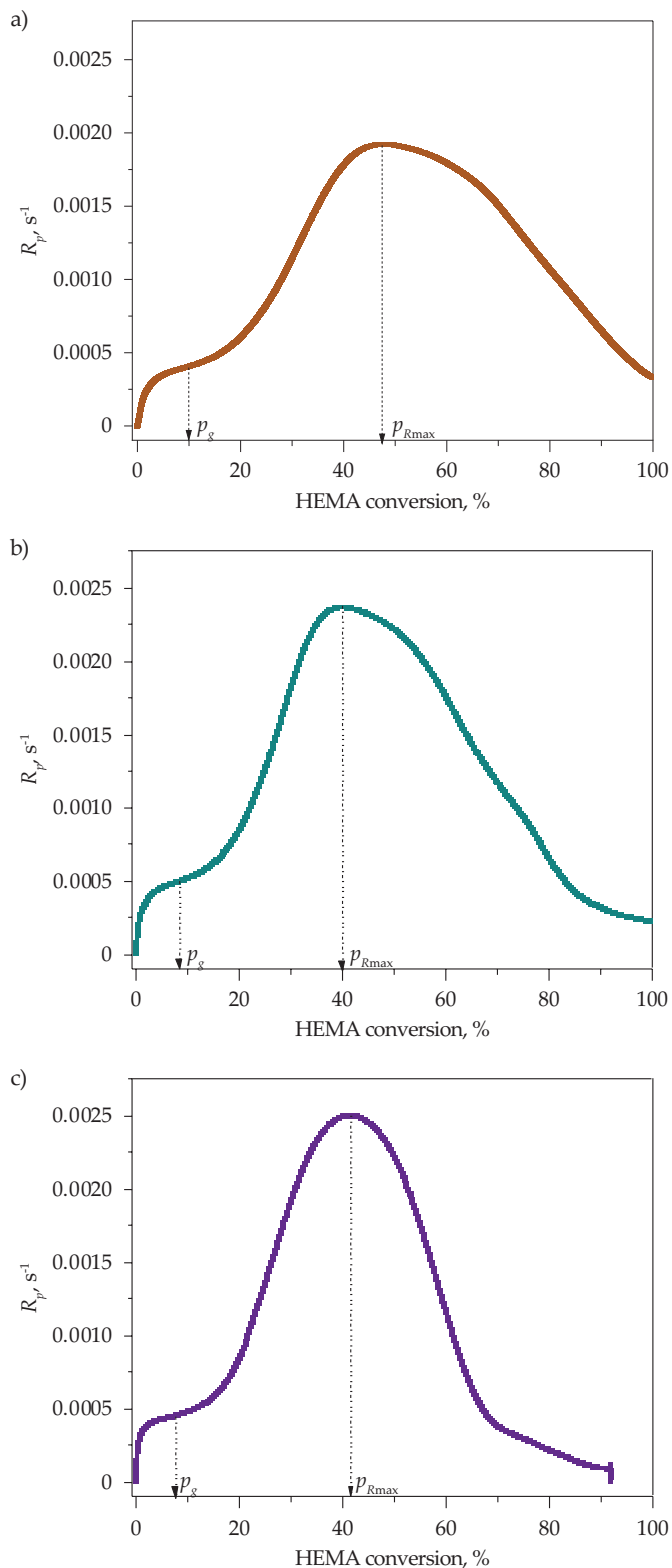
a)

b)

c)

Fig. 4. Dependence of HEMA photopolymerization rate (R_p) on the degree of conversion (p) for systems with different photoinitiator content: a) 0.1 wt%, b) 0.2 wt%, c) 0.5 wt%
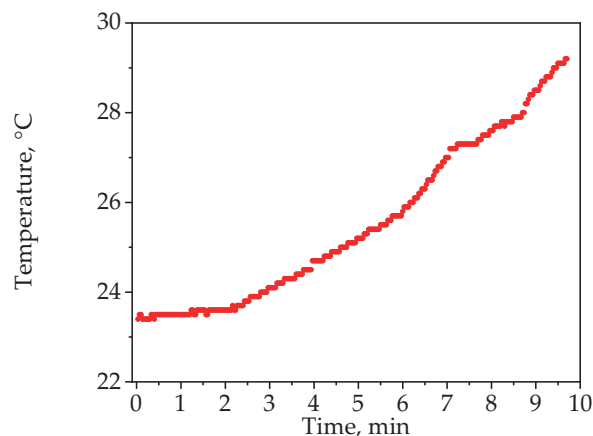

Fig. 5. Temperature during the UV-photopolymerization of HEMA

not contain a layer of liquid (reactants) on the surface. Therefore, it was considered that they are sufficiently cross-linked (cross-linking „+" in Table 2).

The reference sample (H025) was a hydrogel obtained by cross-linking photopolymerization of HEMA with PEGDA. Three types of hydrogels were obtained, i.e., (I) HEMA + PEGDA; (II) S-PHEMA+PEGDA; (III) S-PHEMA+PEGDA+NE. Hydrogels contained the same amount of cross-linking monomer PEGDA700 (Table 2). The H025 sample (type I) contains 75 wt% of water and 25 wt% HEMA. After UV-cross-linking, it was white and flexible. Replacing the HEMA monomer with S-PHEMA solution in the composition of the ingredients (in the same amount) first required a reduction of the photoinitiator dose (to 0.85 wt%), because at 1 wt. part of O2959 a very rigid sample was obtained. Despite this, the sample HS25 (type II) was rigid as well. Therefore, in the next step, the content of distilled water was increased (up to 80 wt%) and the amount of S-PHEMA was reduced (5 wt%), while maintaining 0.85 wt. part of photoinitiator. Using S-PHEMA solution instead of pure HEMA lowers demand for monomer and photoinitiator which is economic benefit. The HS20 hydrogel was elastic. Subsequent attempts included introducing nettle extract to the hydrogel formula (type III). In preliminary studies, it was attempted to introduce a more significant amount of nettle extract (0.5 or 1 wt part /100 wt parts of water and S-PHEMA), however, even at a very high photoinitiator dose (up to 5 wt parts), crosslinking photopolymerization occurred only partially (on the surface a large number of unreacted components remained). Only at 0.3 wt part of nettle extract, cross-linked and elastic hydrogel materials were obtained (Table 2).

The second aim of the presented research was to show the effect of photoinitiator dose on the process of cross-linking photopolymerization of water-S-PHEMA systems containing the highest possible concentration of nettle extract (i.e., 0.3 wt%). The analysis of FTIR spectra (Fig. 6) showed that in the reference sample H025 there are no unreacted C=C bonds coming from the HEMA

T a b l e 2. Morphology of hydrogels

Hydrogel (type/symbol)		Cross-linking/Flexibility	Images
I	H025	+/+	
II	HS25	+/-	
	HS20	+/+	
III	HS20N/0.85	+/+	
	HS20N/1.5	+/+	
	HS20N/2.5	+/+	
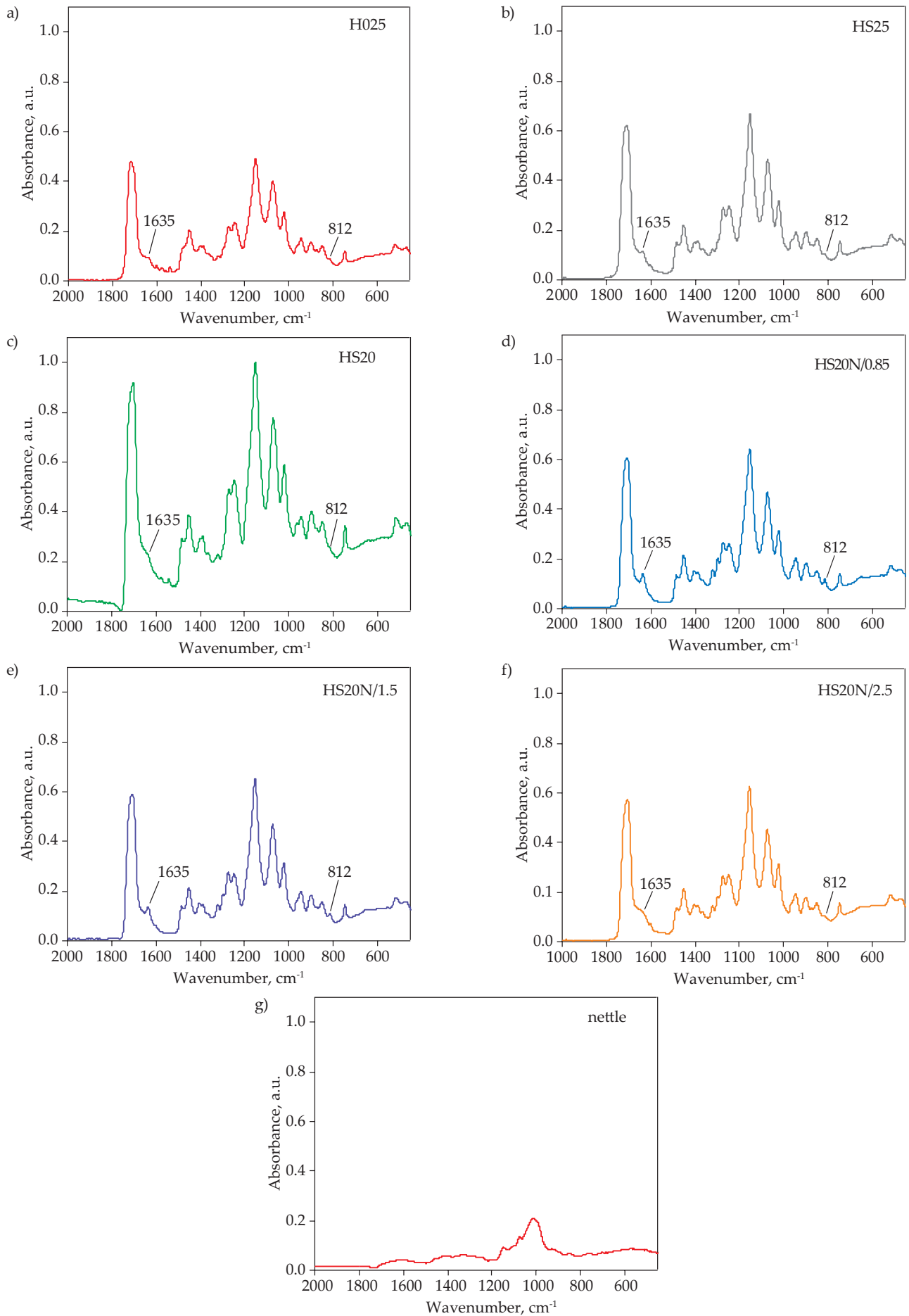
Fig. 6. FTIR spectra: a–f) hydrogels, and g) nettle extract
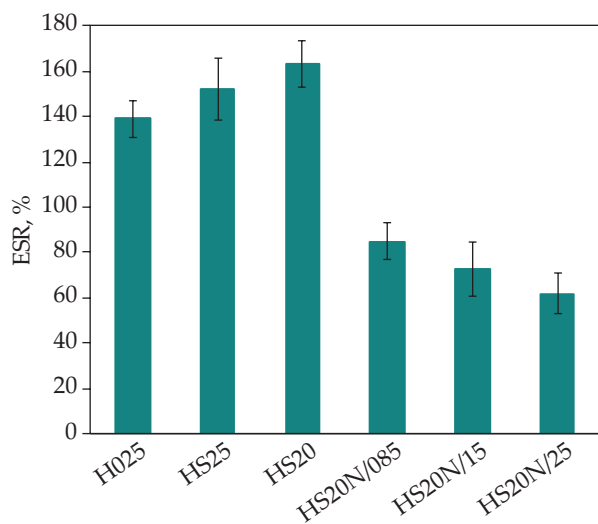
Fig. 7. Equilibrium swelling ratio of hydrogels

Fig. 8. MDSC thermograms of hydrogels obtained using HEMA (H025) and S-PHEMA (HS25)

monomer or cross-linking monomer (Fig. 4a). On the other hand, the HS25 sample shows bands characteristic of C=C bonds, although with relatively low absorbance (Fig. 6b). The use of a lower concentration of S-PHEMA, i.e., 20 wt% (which, as in any case, contains ca. 50% by weight of the linear PHEMA) and the same photoinitiator dose gave better results as far as unreacted monomers are concerned; namely, the disappearance of the characteristic bands at wave numbers 812 cm^{-1} and 1635 cm^{-1} (Fig. 6c).

On the other hand, in samples containing nettle extract and a small photoinitiator dose (0.85 or 1.5 wt parts), sharp bands characteristic of unsaturated bonds was visible (Fig 6d, e). However, their absorbance decreased with increasing photoinitiator dose. In the FTIR spectrum of the HS20/N2.5 sample, these bands were absent (Fig. 6f). This means that the components of the nettle extract strongly affect the cross-linking photopolymerization process by extinguishing the excited states of the photoinitiator. The nettle extract used in the research is standardized in terms of the content of silica and polyphenols. As it is well known, polyphenols have an antioxidant effect, so they are scavengers of free radicals. For this reason, nettle hydrogel systems require an increased dose of photoinitiator.

Absorption properties of the obtained hydrogels are shown in Figure 7.

As it turned out, the highest ESR results were obtained for hydrogels based on S-PHEMA, compared to the reference sample. This study showed the indisputable advantage of S-PHEMA-based hydrogels. The very high ESR value for the HS20 sample (163%) is the result of the presence of linear poly(2-hydroxyethyl methacrylate) in the formation of the HEMA-PEGDA network. In this case, a polymer network of the semi-IPN type is formed. However, the introduction of nettle extract into the system negatively affects the ESR values. For samples HS20 and HS20/N085, which differ only in that the latter contains 0.3 wt part nettle extract, a significant decrease in ESR from 163 to 85% was recorded. This may be because in
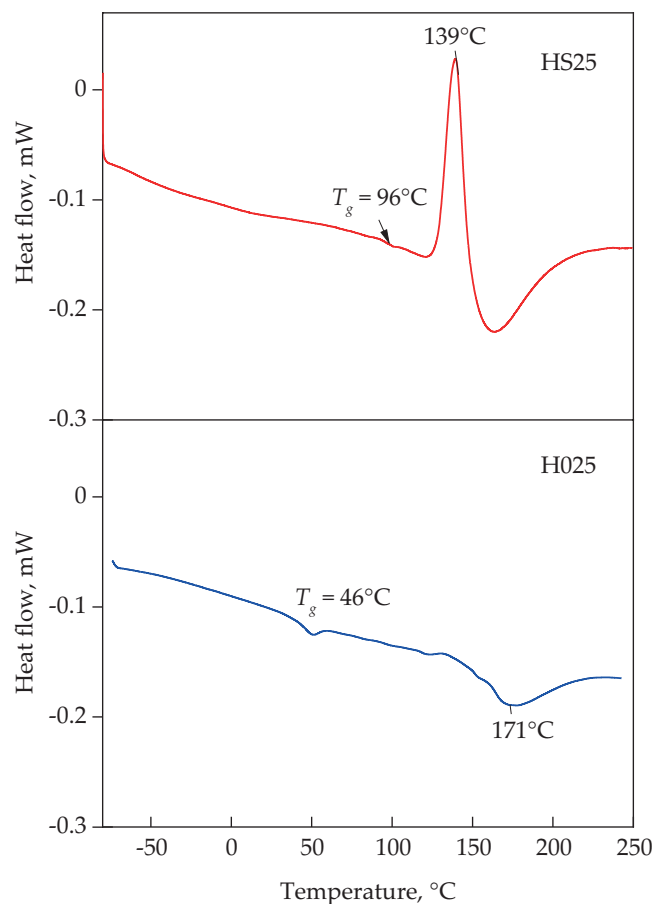
the case of HS20/N085 unreacted monomers have been detected so that the network structure is not as dense as in HS20. In addition, the generally reduced ESR values for hydrogels containing nettle result from the content of hydrophobic components, especially silicon compounds. Moreover, the ESR values decrease further with the increase of the photoinitiator dose in the system. This is due to the formation of a denser polymer network (more network nodes), which makes the spaces between the nodes smaller and less loosely bound water is contained in them. Additionally, a high degree of cross-linking, resulting in a more compact structure of the hydrogel, is associated with reduced mobility of polymer chains, which in turn causes a decrease in water content.

The ESR values of hydrogels are also related to their supermolecular structure. Due to the degree of order of the structure, hydrogels are distinguished into amorphous, semi-crystalline, crystalline, and supramolecular hydrogels. The MDSC thermograms of hydrogels are given in Figure 8 and Figure 9.

In the case of H025 sample, the MDSC thermographs shows T_g (ca. 46°C) as well as melting of the crystalline phase with a peak temperature (T_{mc}) of 171°C. The melting enthalpy of the crystalline phase is relatively small (ca. 31 J/g). This result indicates that there is a polymer with a low degree of crystallinity in this system. In the case of a system containing S-PHEMA in place of HEMA,
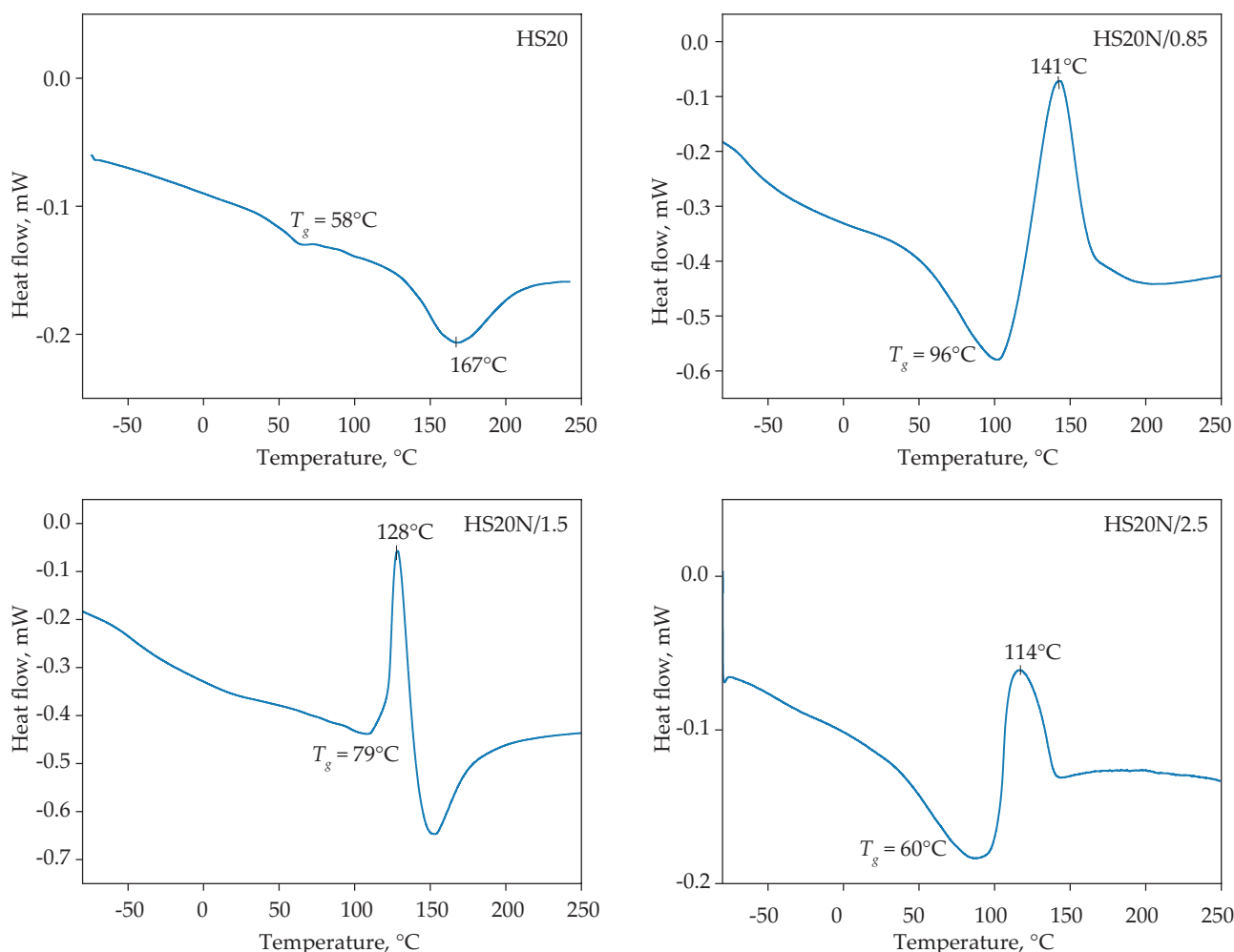
Fig. 9. MDSC thermograms of hydrogels obtained using S-PHEMA (20 wt%) and containing nettle extract, and different amount of photoinitiator

T_g is slightly higher (96°C). On the other hand, the peak indicating the so-called cold crystallization is very pronounced (139°C). This is a characteristic feature of a crystalline polymer with a high degree of amorphous phase. The endothermic peak associated with the melting of the crystalline phase occurs immediately after the cold crystallization peak. The glass transition temperature for a system with a lower content of S-PHEMA (HS20) is 58°C. Also visible is the characteristic endothermic peak associated with the melting of the crystalline phase. In this case, there is no cold crystallization (as for HS25), so the sample is characterized by a smaller share of the amorphous phase. In contrast, samples containing nettle extract show a wide glass transition region. The T_g values decrease with the photoinitoator dose, due to the overall increase in cross-link density. The decrease in the share of the amorphous phase is also characteristic (smaller area under the exothermic peak of cold crystallization).

These properties of hydrogels affect their mechanical strength, i.e., tensile strength and Young's modulus, which are presented in Figure 10.

As can be seen, the highest tensile strength and Young's modulus results (0.84 MPa and 0.5 MPa respectively) were recorded for the reference sample H025,

which was characterized by the highest degree of crystallinity. The sample, which contained S-PHEMA (HS25) instead of HEMA, could not be tested because the fittings were destroyed during their preparation. In general, S-PHEMA-based hydrogels showed significantly lower tensile strength due to the lower cross-linking density of semi-IPN systems compared to those based on
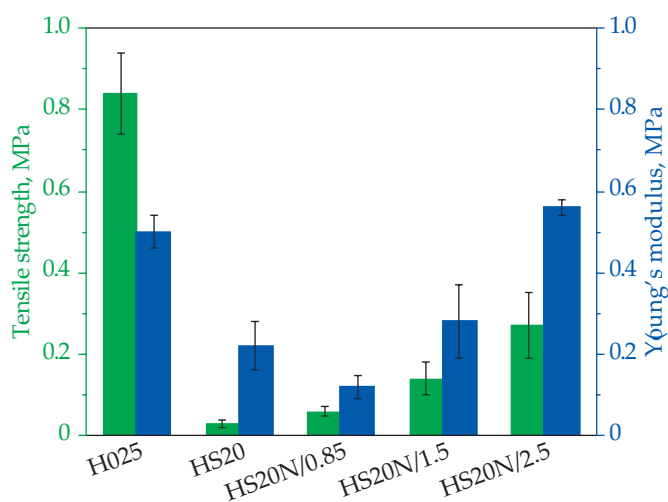

Fig. 10. Mechanical properties of hydrogels

HEMA monomer (half of the HEMA monomer is present in the form of a linear polymer, and half is in creating the HEMA-PEGDA network). However, as the photoinitiator content increases in S-PHEMA-based systems containing nettle extract, the tensile strength and Young's modulus increase due to the more efficient course of the photo-crosslinking process [43].

CONCLUSIONS

Hydrogels based on poly(2-hydroxyethyl methacrylate) solutions crosslinked using poly(ethylene glycol) diacrylate and containing nettle extract were successfully prepared. It has been proven that replacing the monomer with a polymer solution previously obtained in the bulk photopolymerization process allows for increasing the absorption capacity of the hydrogel but deteriorates its mechanical properties. It is also important to use more water in such hydrogel preparations and limit the addition of monomer. It has also been proven that it is possible to obtain hydrogels containing nettle extract, so potentially such systems would have a wound-healing effect. However, the content of nettle extract in the hydrogel preparation is relatively small and requires an increased dose of photoinitiator.

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