

Technological Properties of Polymers Obtained from Humic Acids of Ukrainian Lignite

Vladimir Lebedev¹, Denis Miroshnichenko¹, Zhang Xiaobin¹, Serhiy Pyshyev², Savchenko Dmytro¹

¹ National Technical University «Kharkiv Polytechnic Institute», 61002, Kirpychova str.2, Kharkiv, Ukraine

² Lviv Polytechnic University, 79013, Bandera str. 12, Lviv, Ukraine

Received February 7, 2021; Accepted May 31, 2021

Abstract

Graphic and mathematical dependences of the effect of humic acids (0–15%) obtained from 3 coal samples ($V^d=29.1-43.7\%$; $C^{daf}=60.71-80.83\%$; $O^{daf}_d=10.9-29.12\%$) and the gelation time (0–15 minutes) for the dynamic viscosity of the hydrogel. The influence of the content of humic acids on the melting point, degradation temperature and gelatinization time of hydrogels has been established. It has been determined that an increase in the size of coal particles to 1.0 mm in humic acids leads to a decrease in the processes of structure formation of the hydrogel.

Keywords: Coal; Lignite; Humic acids; Hydrogels; Equations.

1. Introduction

One of the most important areas of modern research in the field of polymer materials is the field of obtaining and studying the properties of polymer hydrogels. Hydrophilic polymers with large volumes of water absorption and storage are known as hydrogels, or superabsorbents [1]. The hydrogel is a three-dimensionally crosslinked and swollen polymer in water and does not dissolve in it. The water-holding capacity of hydrogels is due to the presence of hydrophilic groups along the polymer chain, such as OH, -CONH, -CONH₂, -COOH [2]. They can be composed of natural substances and synthetic high molecular weight materials. Due to a complex of unique properties, these "smart" materials for targeted delivery of useful and functional substances are in demand and promising polymer compositions for many industries: medical, cosmetic, pharmaceutical, agricultural. Hydrogels are widely used for various biomedical applications - tissue engineering, molecular imprinting, immune isolation, dressings, drug delivery, and the like. In addition, a biodegradable, non-toxic, low cost starch hydrogel can be produced. Acrylamide-based hydrogels are widely used in medicine, agriculture, and other industries. Hydrogel masks and face patches have become a new trend in the field of polymer hydrogels application. Their main function is to intensively moisturize the skin, and almost all hydrogel masks and patches also start detoxification processes - they get rid of toxins and toxins that accumulate in human skin. The hydrogel base of masks and patches adheres well to the surface of human skin and creates conditions similar to the greenhouse effect, which further contributes to effective skin cleansing. In addition, the created microclimatic system of the skin accelerates blood circulation and thereby ensures effective penetration into the deep layers of the skin and improves the absorption of beneficial active substances. Hydrogel materials containing collagen, silver or gold nanoparticles, clay minerals such as kaolinite, bentonite, etc., deserve the attention of cosmetologists. In view of this, research on the development and study of effective polymer hydrogel materials is in great demand today.

To date, most studies of hydrogels based on three-dimensional polymer networks are conducted in the direction of studying various materials for cosmetology, pharmacy, and medicine [1-3].

As a result of the studies carried out in [4], the area of formation in the structure of the gel of macromolecular aggregates "gelatin - sodium alginate", providing the gel with extreme

values of elastic-visco-plastic characteristics, was established. Among all developments in the field of gene-activated hydrogels, the greatest progress has been achieved precisely in the treatment of patients with skin lesions [5–10]. Thus, Cardium Therapeutics (USA) and Tissue Repair Company (USA) have created a gene-activated hydrogel based on collagen and an adenoviral construct carrying the platelet-derived growth factor-BB (PDGF-BB) gene for the treatment of patients with chronic skin ulcers caused by diabetic neuropathy [5–6]. Another research group in a model of in vivo skin wound healing compared the use of sodium alginate hydrogels containing either plasmid DNA carrying the SDF-1 gene or the recombinant SDF-1 protein [7]. Several more studies are in the early stages and are focused on evaluating the efficiency of delivery of marker gene constructs by various hydrogels. In particular, it has been shown that an alginate hydrogel is capable of providing delivery of lentiviral vectors [8], as well as plasmid DNA [9–10]. In general, based on published research results, it can be confidently asserted that most biocompatible, non-toxic hydrogels that do not negatively affect nucleic acids are capable of performing the function of a carrier matrix for gene constructs. Practically in all scientific studies of polymer hydrogels, it is noted that the physicochemical properties and compression resistance of hydrogels, which, in turn, are determined by the nature of the polymer, the degree of structure formation, and the polymer: water ratio, determine the areas of their most effective application [11–12]. Therefore, obtaining and studying the effect of various factors on the characteristics of polymer hydrogels is an important and urgent task of modern polymer chemistry [13].

On the other hand, in the world (including in Ukraine) there are significant deposits of lignite (brown coal), which contains humic acids and can be a component of raw materials for the production of hydrogel materials. Currently, lignite have a very limited use due to poor technological characteristics (high ash, water and sulfur contents). Lignite are proposed to be used in the oxidative desulfurization process [14–17], to obtain components of boiler fuels or bitumen [18], in gasification processes [19]. However, the direction of application of brown coal seems to be the most promising for the extraction of humic acids and subsequent production of hydrogel materials.

The purpose of this article is to investigate the features of the effect of humic acids on the processes of structure formation in polymer hydrogels based on gelatin.

2. Experimental part

2.1. Raw materials

Humic acid was obtained according to [20]. The essence of the method consists in processing an analytical fuel sample with an alkaline solution of sodium pyrophosphate, subsequent extraction of the sample with a solution of sodium hydroxide, precipitation of humic acids with an excess of mineral acid, and determination of the mass of the resulting sediment.

In total, three samples of humic acids were used, obtained from three samples of brown coal. The results of determining the quality of brown coal samples are shown in Tables 1–4.

To obtain polymers, we used food gelatin grade P-11 according to [21], the main quality indicators are given in Table 5.

Table 1. Proximate analysis of coal, %

Sample	W ^a	A ^d	S ^d _t	V ^d
1	16.8	48.7	2.50	29.1
2	8.1	8.3	1.87	43.7
3	30.6	36.7	4.00	43.7

Table 2. Ultimate analysis of coal, %

Sample	C ^{daf}	H ^{daf}	N ^{daf}	S ^d _t	O ^{daf} _d
1	80.83	4.48	1.29	2.50	10.9
2	68.10	4.57	1.35	1.87	24.11
3	60.71	4.87	1.30	4.00	29.12

Table 3. Total mass fraction and yield of free humic acids

Sample	(HA) ^{daf_t} , %	(HA) ^{daf_r} , %
1	87.60	79.44
2	49.66	44.27
3	82.94	75.30

Table 4. Chemical composition of coal ash, %

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SO ₃
1	70.08	9.83	3.24	0.88	5.43	0.77	0.90	5.90
2				No data				
3				No data				

Table 5. Quality indicators of P-11 gelatin

Nº	Indicator name	Characteristics and norm
1	Appearance	Grains
2	Colour	Light yellow
3	Smell	Absent
4	Taste	tasteless
5	Particle size, mm, no more	10
6	Mass fraction of particles less than 0.5 mm, %, no more	30
7	Duration of dissolution, min, no more	25
8	The indicator of the activity of hydrogen ions in an aqueous solution of gelatin with a mass fraction of 1%, units, pH	from 5 to 7
9	Mass fraction of moisture, %, no more	16
10	Mass fraction of ash, %, no more	2.0
11	Strength of jelly with a mass fraction of gelatin 10%, N, not less	11
12	Dynamic viscosity of a solution with a mass fraction gelatin 10%, mPa·s, not less	20.0
13	Melting point of jelly with mass fraction gelatin 10%, °C, not less	32
14	The transparency of the solution with a mass fraction of gelatin 5%, %, not less	45
15	Impurities, %, no more	Not allowed
16	Sulfurous acid in terms of SO ₂ , %, no more	0.075
17	Mesophilic aerobic and facultative anaerobic microorganisms, CFU, in 1 g of gelatin, no more	1·10 ⁵
18	Coliform bacteria (coliforms) in 0.01 g of gelatin	Not allowed
19	Pathogenic microorganisms, including salmonella, in 25 g	Not allowed
20	Gelatin-thinning bacteria, CFU, in 1 g of gelatin, no more	2·10 ²

2.2. Experimental techniques

Hydrogels from gelatin and humic acids were prepared as follows. First, a 10% gelatin solution was made in distilled water at a temperature of 90–100°C. After that, by mixing, solutions with humic acids were obtained, in which the concentration of the latter was 0, 5, 10 and 15%.

Samples were taken from the resulting solutions after 5, 10, and 15 minutes to determine the viscosity, melting point, degradation temperature, and gelation time of polymer hydrogels.

The viscosity was determined according to [22]. The method is based on determining the viscosity of a gelatin solution at a certain temperature and a drop in viscosity after a certain time of exposure on a capillary viscometer.

The melting point was determined according to [22]. The method is based on determining the temperature at which the gelatin jelly turns into a fluid state.

The destruction temperature was determined according to [23]. The destruction temperature is determined on a brass disc with a diameter of 50 mm and a thickness of 20 mm, equipped with a tinder thermometer. The temperature range of destruction is determined by the nature of the change in the appearance of the polymer during heating. The destruction

temperature is recorded at the beginning of intensive darkening of the polymer material placed on the surface of the heated brass disk, which is accompanied by the intense release of gaseous combustion products and ends with the carbonization of the polymer sample with the formation of black coke residue.

The determination of the gelation time took place in accordance with [24]. The essence of the method is as follows. Prepare the resin mixture at 25°C with the specified amount of the standard accelerator and initiator. The resulting mixture is placed in a test tube of established dimensions, which is immersed in a bath with a temperature of 25°C.

The instrument, which has a minimal effect on the viscometric properties of the mixture, is used to determine the exact time at which the viscosity reaches 50 Pa·s (500 poise) (conditional viscosity corresponding to the onset of the gelation state). The total time from the moment of adding the accelerator and initiator to the moment at which the viscosity reaches a value of 50 Pa·s is conventionally called «Gelatinization time at 25°C».

3. Results and discussion

Figures 1–3 show graphical dependences of the dynamic viscosity of hydrogel solutions on the concentration of humic acid in them, obtained from various coal samples, and on the exposure time. The dependence of dynamic viscosity on indicators characterizing the degree of metamorphism (V^d , C^{daf} , O^{daf}_d) of coals is shown in Fig. 4-6. Table 6 shows the mathematical equations describing the graphical dependencies shown in Fig. 4-6, as well as their statistical assessment.

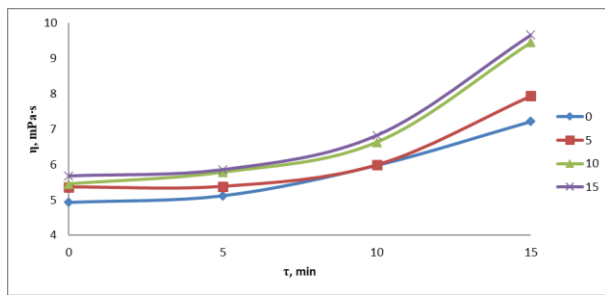


Fig. 1 Dependence of the dynamic viscosity of the hydrogel on the content of humic acid obtained from sample No. 1

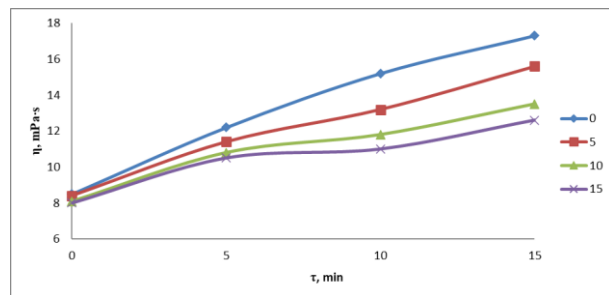


Fig. 1 Dependence of the dynamic viscosity of the hydrogel on the content of humic acid obtained from sample No. 2

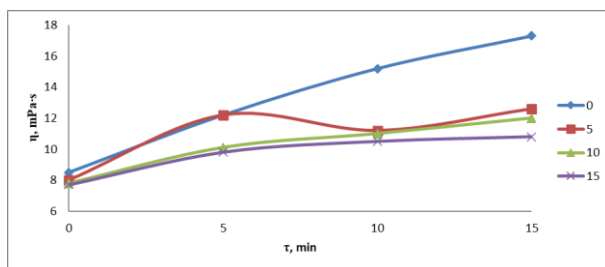


Fig. 3 Dependence of the dynamic viscosity of the hydrogel on the content of humic acid obtained from sample No. 3

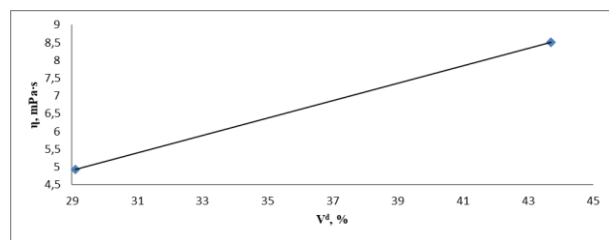


Fig. 4 Influence of the release of volatiles in coal on the dynamic viscosity of gelatin

Table 6. Mathematical equations and statistical estimation

No.	Equation type	R ²
1	$\eta = 0.2445 \cdot V^d - 2,1855$	1,0000
2	$\eta = -0.1887 \cdot C^{daf} + 20,4970$	0,8682
3	$\eta = 0.2111 \cdot O_d^{daf} + 2,7978$	0,9292

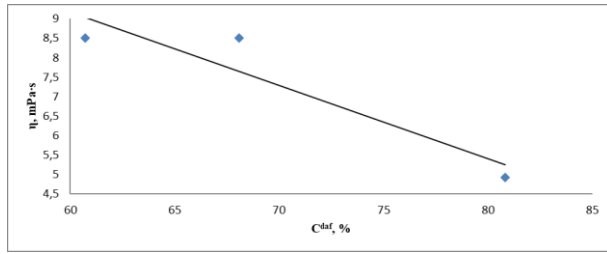


Fig. 5. Influence of the carbon content in coal on the dynamic viscosity of gelatin

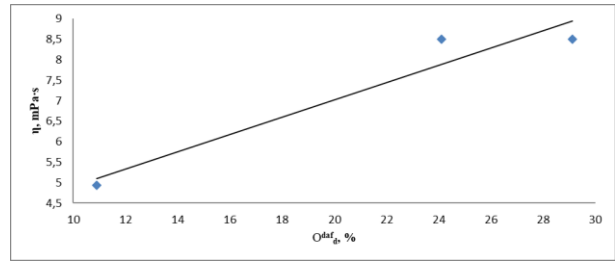


Fig. 6. Influence of the oxygen content in coal on the dynamic viscosity of gelatin

Analyzing the graphical and mathematical relationships, it can be concluded that an increase in the degree of metamorphism of the initial coals, expressed by an increase in the yield of volatile substances and the oxygen content, leads to a decrease in the dynamic viscosity of the hydrogel.

It is of interest to determine, in addition to the factors describing the degree of coal metamorphism, the influence of the exposure time and the concentration of humic acids.

Table 7 shows the mathematical equations describing the influence of the degree of metamorphism, exposure time and concentration of humic acids, in Fig. 7-9 graphical dependencies showing the relationship between the actual and calculated values of dynamic viscosity, determined by formulas 4-6.

Table 7. Mathematical equations and statistical estimation

No.	Equation type	Statistical estimation		
		R ²	R	SE, mPa·s
4	$\eta = -4.98244 - 0.11185 \cdot HA + 0.31978 \cdot \tau + 0.33934 \cdot V^d$	0.841	0.917	1.37
5	$\eta = 25.62277 - 0.11185 \cdot HA + 0.31978 \cdot \tau - 0.24939 \cdot C^{daf}$	0.733	0.856	1.77
6	$\eta = 2.14487 - 0.11185 \cdot HA + 0.31978 \cdot \tau + 0.28304 \cdot O_d^{daf}$	0.774	0.880	1.63

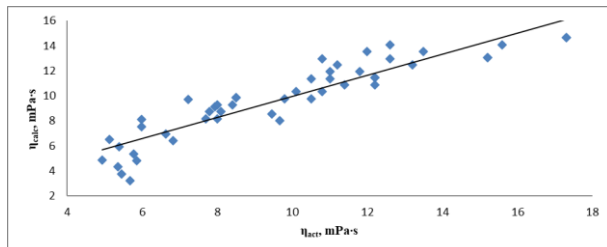


Fig. 7. Graphical relationship between actual and calculated values of dynamic viscosity obtained according to equation 4

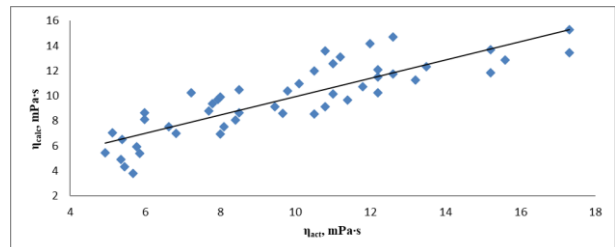


Fig. 8. Graphical relationship between actual and calculated values of dynamic viscosity obtained according to equation 5

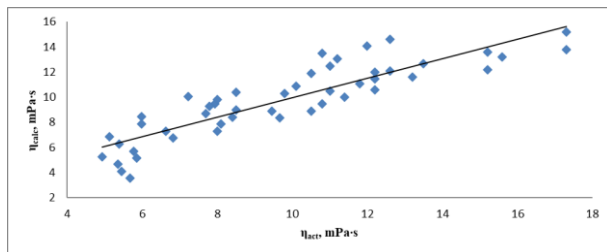


Fig. 9. Graphical relationship between actual and calculated values of dynamic viscosity obtained according to equation 6

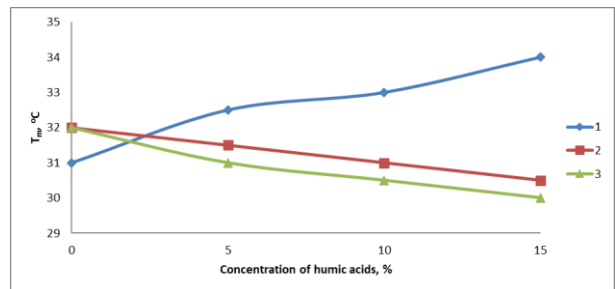


Figure 10. Graphical dependence of the melting point of the hydrogel on the concentration of humic acids in it

In Fig. 10 shows a graphical dependence of the melting point of a hydrogel with a concentration of humic acids from 0 to 15%. Analyzing the above graphs, it can be concluded that an increase in the concentration of humic acids, depending on the properties of the original coals, leads to both an increase (sample 1) and a decrease (sample 2 and 3) of the hydrogel melting temperature. In Fig. 11 shows a graphical dependence of the degradation temperature of the hydrogel on the concentration of humic acids in it.

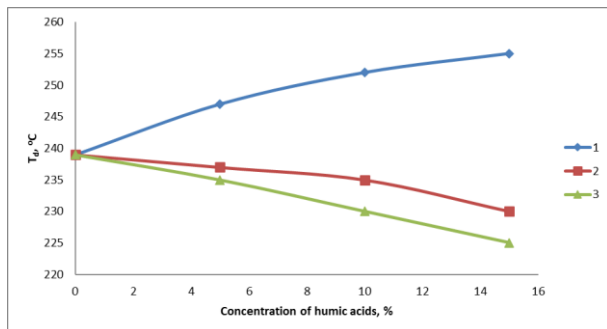


Fig. 11. Graphical dependence of the temperature of hydrogel destruction on the concentration of humic acids in it

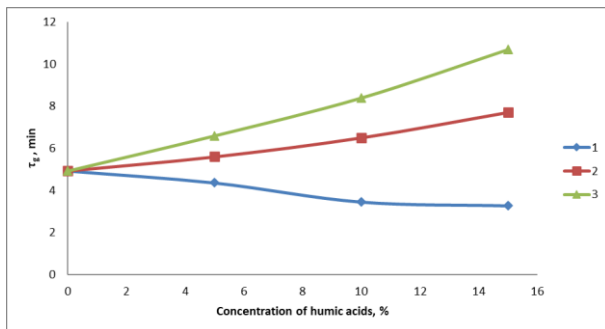


Fig. 12. Graphical dependence of the gelatinization time of the hydrogel on the concentration of humic acids in it

Analyzing the graphs presented, it can be concluded that an increase in the concentration of humic acids, depending on the properties of the original coals, leads to both an increase (sample 1) and a decrease (samples 2 and 3) of the hydrogel destruction temperature.

In Fig. 12 shows a graphical dependence of the gelatinization time of the hydrogel on the content of humic acids in it. Analyzing the graphs presented, it can be concluded that an increase in the concentration of humic acids, depending on the properties of the initial coals, leads to both an increase (sample 2, 3) and a decrease (sample 1) of the gelatinization time of the hydrogel.

Summarizing the data on the effect of humic acids on the processes of structure formation in polymer hydrogels based on gelatin, it is important to emphasize its different nature for different hydrogels. So, for hydrogels with the addition of humic acids of sample 1, an intensifying structure-forming effect is clearly visible: the viscosity and the temperature of destruction increase with a decrease in the gelation time. At the same time, in hydrogels with the addition of humic acids in samples 2 and 3, an opposite pattern is observed, and they are inhibitors of the processes of structure formation in gelatin hydrogels. To clarify the reasons for such a different nature of the effect of the studied humic acids, microscopic studies of the obtained hydrogels were carried out, the results of which are shown in Fig. 13.

From the analysis of the obtained micrographs of the studied gelatin hydrogels with different contents of samples of humic acids, the different nature of the stay of humic acids in gelatin hydrogels was determined for three types of samples under study. Thus, sample 1 is characterized by the formation of a homogeneous transparent hydrogel, which, with an increase in the content of humic acids, only changes its color to a more yellow one. At the same time, for hydrogels obtained with the addition of samples of 2 and 3 humic acids, the presence of larger particles of coal (up to 1.0 mm) in the mass of samples is observed. In our opinion, it is the presence of larger coal particles in samples 2 and 3 that causes a decrease in the processes of structure formation in gelatin hydrogels by preventing the formation of a spatial network structure in them. On the contrary, the introduction of humic acids of sample 1 into the composition of gelatin hydrogels, for which the presence of particles of coal residues of various degrees of dispersion is not observed, causes an increase in the processes of structure formation.

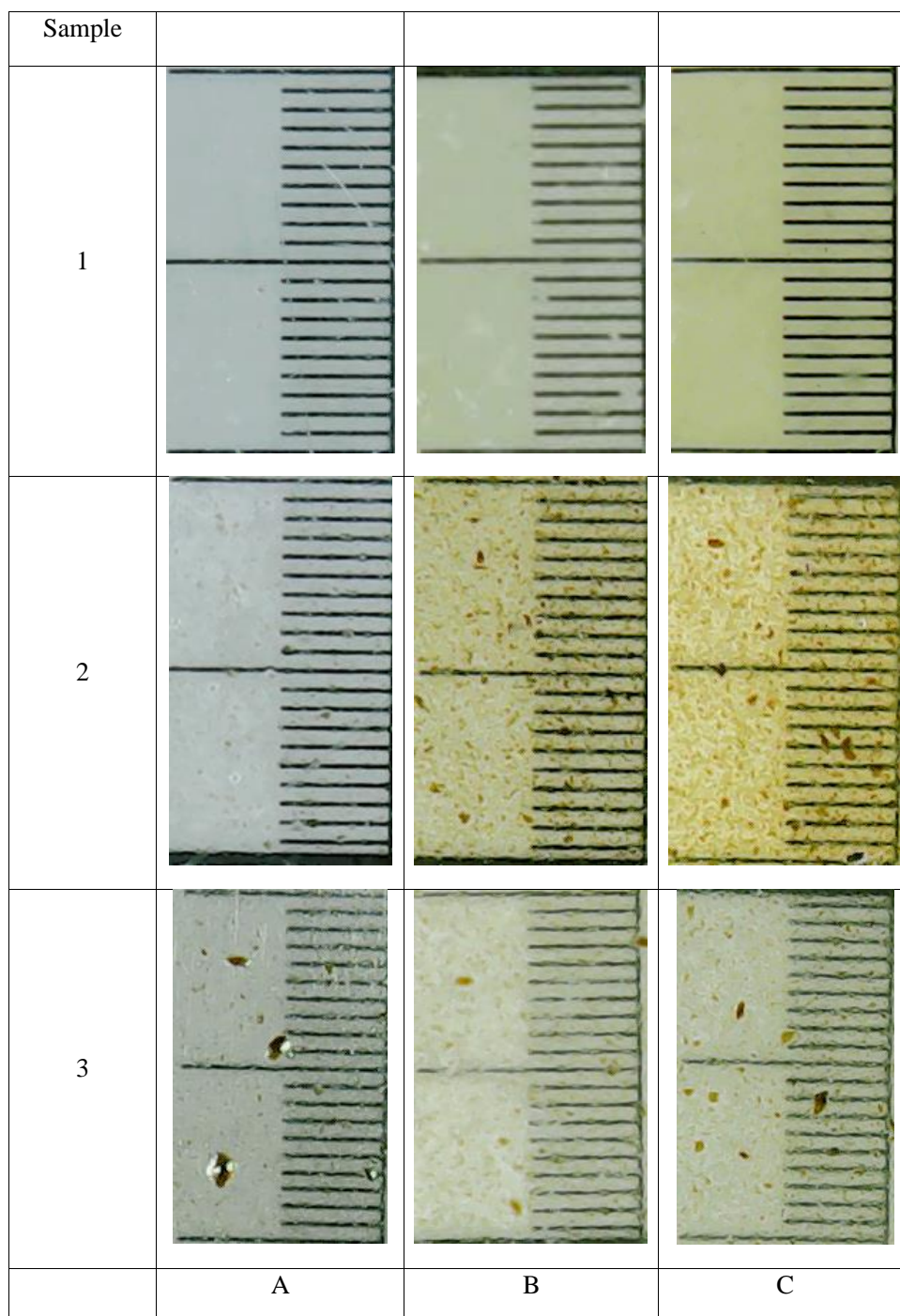


Fig. 13. Micrographs (DIV = 1 mm) of the investigated polymer hydrogels of gelatin with different content of humic acid: A - polymer hydrogel of gelatin with 5% humic acids; B - polymer hydrogel of gelatin with 10% humic acids; C - polymer hydrogel of gelatin with 15% humic acids

4. Conclusions

Graphic and mathematical dependences of the effect of humic acids (0–15%) obtained from 3 coal samples ($V^d=29.1-43.7\%$; $C^{daf}=60.71-80.83\%$; $O^{daf}_d= 10.9-29.12\%$) and the gelation time (0–15 minutes) for the dynamic viscosity of the hydrogel. The influence of the content of humic acids on the melting point, degradation temperature and gelatinization time of hydrogels has been established. It has been determined that an increase in the size of coal

particles to 1.0 mm in humic acids leads to a decrease in the processes of structure formation of the hydrogel.

Acknowledgment

The authors are grateful for the financial support of the China Scholarship Council (No.201908100012).

Symbols

W^a	moisture contents, %;	Fe_2O_3	content of iron oxide, %;
A^d	ash content, %;	MgO	content of magnesium oxide, %;
S_t^d	content of sulfur, %;	CaO	content of calcium oxide, %;
V^d	volatile matter, %;	Na_2O	content of sodium oxide, %;
C^d	content of carbon, %;	K_2O	content of potassium oxide, %;
H^d	content of hydrogen, %;	SO_3	content of sulfur oxide, %;
O^d	content of oxygen, %;	η	dynamic viscosity, mPa·s, %;
$(HA)^{daf}_t$	total mass fraction of humic acids, %;	T_m	melting temperature, °C;
$(HA)^{daf}_f$	yield of free humic acids, %;	T_d	decomposition temperature, °C;
SiO_2	content of silicon oxide, %;	T_g	gelation time, min.
Al_2O_3	content of aluminium oxide, %;		

References

- [1] Enas MA. Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research*. 2015. No 6. P. 105-121.
- [2] Zavan B, Cortivo R, and Abatangelo G. *Hydrogels and Tissue Engineering*. Springer-Verlag. Italia, 2009.
- [3] Chobit MR, Bilozir RM, Tokarev VS. Obtaining complex polyacrylamide hydrogels as a basis for cosmetics. *Bulletin of Lviv Polytechnic National University*. 2017. P. 310–318.
- [4] Voronko NG, Derkach SR, Belyaevsky AT. Structural properties of food multicomponent gels according to the method of scanning electron microscopy. *Bulletin of the Moscow State Technical University*. 2004. №1.
- [5] Mulder G, Tallis AJ, Marshall VT. Treatment of nonhealing diabetic foot ulcers with a platelet-derived growth factor gene-activated matrix (GAM501): results of a phase 1/2 trial. *Wound Repair Regen*. 2009. N 17(6). 772.
- [6] Blume P., Driver V.R., Tallis A.J., et al. Formulated collagen gel accelerates healing rate immediately after application in patients with diabetic neuropathic foot ulcers. *Wound Repair Regen*. 2011. 19(3): 302-8.
- [7] Rabbany SY, Pastore J, Yamamoto M. Continuous delivery of stromal cell-derived factor-1 from alginate scaffolds accelerates wound healing. *Cell Transplant* 2010; 19(4): 399-408.
- [8] Stilhano RS, Madrigal JL, Wong K. Injectable alginate hydro-gel for enhanced spatiotemporal control of lentivector delivery in murine skeletal muscle. *J. Control Release* 2016; 10: 237:42-9.
- [9] Wegman F, Bijenhof A, Schuijff L. Osteogenic differentiation as a result of BMP-2 plasmid DNA based gene therapy in vitro and in vivo. *Eur. Cell Mater*. 2011; 15(21): 230-42.
- [10] Kong HJ, Kim ES, Huang YC. Design of biodegradable hydro-gel for the local and sustained delivery of angiogenic plasmid DNA. *Pharm Res*. 2008; 25(5):1230-8.
- [11] Wang Ch-S, Virgilio N, Wood-Adams PM, Heuzey MC. A gelation mechanism for gelatin/poly-saccharide aqueous mixtures. *Food Hydrocolloids*, 2018; 79: 462-472.
- [12] Duan B, Hockaday LA, Kang KH, Butcher JT. 3D bioprinting of heterogeneous aortic valve conduits with alginate/gelatin hydrogels. *J. Biomed. Mater. Res. A.*, 2013; 101: 1255–1264.
- [13] Lebedev V, Tikhomirova T, Savchenko D, Lozovitsky A, Litvinenko E. Studying features of gel formation and rheological processes of gelatin-based hydrogels for cosmetology and medicine. *Integrated Technologies and Energy Saving* 2020, 4: 3-10.
- [14] Gunka V, and Pyshyev S. Lignite oxidative desulphurization. Notice 1: process condition selection. *International Journal of Coal Science & Technology* 2014, 1: 62-69.
- [15] Gunka V, and Pyshyev S. Lignite oxidative desulphurization. Notice 2: effects of process parameters. *International Journal of Coal Science and Technology* 2015, 2: 196-201.
- [16] Pysh'yev S, Gunka V, Bratychak M, and Grytsenko Yu. Kinetic regularities of high-sulphuric brown coal oxidative desulphurization. *Chemistry & Chemical Technology* 2011, 1: 107-113.
- [17] Gunka V, Shved M, Prysiashnyi Y, Pyshyev S, Miroschnichenko D. Lignite oxidative desulphurization: notice 3 – process technological aspects and application of products. *International Journal of Coal Science & Technology* 2017, 6: 63-73.

- [18] Gunka V, and Pyshyev S. Technology of oxidative desulphurization of lignite Volodymyr Gunka, Serhiy Pyshyev. *Pet Coal*, 2015; 57(6): 696-704.
- [19] Bielowicz B, Kasiński JR. The possibility of underground gasification of lignite from Polish deposits. *International Journal of Coal Geology* 2014, 131: 304-318.
- [20] Methods for determining the yield of humic acids, GOST 9517–94 (1996).
- [21] Gelatin. Technical conditions, GOST 11293–89 (2001).
- [22] Photographic gelatin. Method for determining viscosity and viscosity drop, GOST 25183.4–82 (1982).
- [23] Podgornaya LP. Theory and methods of research and testing of plastics, adhesives and sealants: textbook. way. / L.P. Podgornaya, G.M. Cherkashyna, V.V. Lebedev. - Kharkiv: Textbook of NTU "KhPI", 2012. - 268 p.
- [24] Unsaturated polyester resins. Methods for determining the time of gelatinization, GOST 22181–91 (1991).

To whom correspondence should be addressed: Dr. Denis Miroshnichenko, ational Technical University «Kharkiv Polytechnic Institute», 61002, Kirpychova str.2, Kharkiv, Ukraine, Russia, E-mail: dvmir79@gmail.com