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Rheological parameters of polymer-silicate gels

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Abstract. Hydrogels, due to their unique properties (they can absorb large amounts of solution, sometimes even several hundred times higher than their initial mass), have found application in many areas of life. Their polymerization rate depends for example on the pH, temperature, composition of the polymerization mixture, amount of the initiators, degree of cross-linking of the polymer and composition of the polymerization mixture.

The results of the kinetic reactions showed that the increased proportion of silicate in the sample causes faster gelation. It was also found that the lower the silicate modulus is, the polymerization reaction starts faster. However, oscillation tests carried out 24 hours after synthesis showed that better elastic properties (higher values of the elastic modulus G') show samples with higher content of polymer in the composition.

1. Introduction

Hydrogel is a type of gel in which the dispersed phase is water, while the disperse (gelling) phase is a polymer. It is a polymer material that swells and retains large amounts of water in its structure. Depending on the properties of polymers, as well as the nature and density of network connections, they can contain different amounts of water. The ability to absorb the water is due to the presence of hydrophilic groups attached to the main chain, while insolubility in water is the result of cross-links between the network chains.

Due to their origin, hydrogels can be divided into natural (collagen, gelatin, polysaccharides) and synthetic, i.e. manufactured artificially. Taking into account the nature of the interaction between the components, hydrogels can be divide into chemical and physical. Physical hydrogels (reversible gels) form a network, but connected by weak hydrogen bonds, ionic bonds or intermolecular interactions. Chemical hydrogels form a spatial network, where polymer chains are connected by permanent covalent bonds and do not degrade without destroying the entire molecule. Such hydrogels are obtained by polymerization and simultaneous cross-linking of multifunctional monomers or in multistage processes involving the synthesis of a polymer containing reactive groups and their subsequent cross-linking. The reaction of polymers with appropriate cross-linking agents and initiators is also used. Such hydrogels are most often obtained by copolymerization of vinyl and divinyl monomers in the presence of redox initiators. As the cross-linking monomers divinyl and acrylic systems (N, N'-methylenebisacrylamide, glycol acrylate etc.) are used [1-4].

Due to the very good absorption properties, good mechanical strength, thermal and chemical resistance and lack of toxicity, hydrogels are used in many areas. They are used in medicine as drug

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delivery systems, hydrogel dressings or even as hybrid organs. In cosmetics they are used for the production of soaps, shower gels, creams etc. They are also used as a medium in cell colonies and for immobilization of cells in laboratory tests. In gardening and forestry they have been used as agrogels. They can also be used to dehumidify the air, as well as in construction as flame retardant gels, most often in combination with a silicate agent, e.g. water glass.

Gelation of the water glass solution occurs when a significant amount of hydrogen ions that weakens the action of Na+ ions and causes the precipitation of silicic acid molecules, will be found in the intermiceral medium. Acids are the fastest coagulating factor, therefore, to be able to control the gelation process, e.g. polyhydric alcohol esters that are slowly hydrolyzed in alkaline solution, are used. The solution may also be the use of salts containing cations of various metals. Silanol groups of alkali silicates react with divalent and trivalent cations to form silanol-metal bridges which then polymerize, releasing hydrogen and giving silicate-metal polymers. Another method of obtaining gels with water glass is based on the use of the properties of vinyl monomers and soluble silicate solutions. In the reaction system, next to the silicic acid precursor, i.e. water glass, and vinyl monomers, following substances are also found:

- a) system of redox initiators that reduces the reaction temperature,
- b) substances cross-linking the obtained polymer,
- c) polycarboxylic acids that cause silicic acid precipitation,
- d) additional modifying substances, if any.

As a result of simultaneous precipitation of silicic gel and cross-linking of vinyl polymers, mineralorganic hydrogels with increased flexibility and durability are formed [5-9].

2. Experimental section

2.1. Materials

Sodium water glasses (WG) R-137, R-145, R-150 with silicate moduli M = 3.2, 2.5 and 2.1 respectively were used as the silicate component. The monomer was a 20 wt% aqueous solution of sodium acrylate (ANa) or potassium acrylate (AK) synthesized in a stoichiometric reaction by neutralization of acrylic acid (AA) with a saturated aqueous solution of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and then diluted to the proper concentration. Potassium persulphate (KPS) and sodium thiosulphate (NTS) were used as the redox initiators and N,N'-methylenebisacrylamide (NNMBA) was used as the cross-linker. All reagents were used without further purification. They are listed in Table 1.

Table 1. Osed chemical substances.				
Name of the substance	Source			
Sodium water glasses (R-137, R-145, R-150)	"Rudniki" Chemical Plant, Poland			
Acrylic acid	Acros Organics, Belgium			
N,N'- methylenebisacrylamide	Acros Organics, Belgium			
Potassium persulphate	Acros Organics, Belgium			
Sodium thiosulphate	POCH LLC, Poland			
Sodium hydroxide	POCH LLC, Poland			
Potassium hydroxide	POCH LLC, Poland			

 Table 1. Used chemical substances.

2.2. Synthesis of polymer-silicate gels

In the first step, mixtures of diluted acrylates (in a mass ratio of AK to ANa 0.8:0.2, 0.5:0.5 and 0.2:0.8) were prepared. Then, 20 wt% aqueous solutions of acrylates were added at a mass ratio of 1:1, 1:2 and 2:1 to the sodium water glass and were stirred on a magnetic stirrer for 5-10 minutes to obtain

a transparent solution. When after this time the sample was still turbid, the composition was removed from further testing. The cross-linker (NNMBA) and system of redox initiators (KPS/NTS) were added in an amount of 0.1 wt% to the sample weight. The polymerization mixture gelled within 15-30 minutes according to the free-radical mechanism. The compositions of the polymer-silicate hydrogels are shown in Table 2.

WG	R-137		R-145		R-150				
Silicate modulus	3.2			2.5		2.1			
Mass ratio of WG:Ax	1:2	1:1	2:1	1:2	1:1	2:1	1:2	1:1	2:1
ANa	-	-	-	+	+	+	+	+	+
AK	-	-	-	-	+	+	+	+	+
A(K:Na) 0.8:0.2	-	-	-	+	+	+	+	+	+
A(K:Na) 0.5:0.5	-	-	-	-	+	+	+	+	+
A(K:Na) 0.2:0.8	-	-	-	-	+	-	+	+	+

 Table 2. List of the prepared polymer silicate hydrogels (+- transparent hydrogel, - - turbid mixture).

2.3. Rheological measurements

An Anton Paar Physica MCR-301 rheometer equipped with a plate-plate (PP25) system was used for all of the rheological measurements. The polymerization kinetics of the tested polymer-silicate hydrogels was measured at variable shear frequencies in the range from 0.1 to 100 Hz for 30 minutes. The measuring gap was set at 0.1 mm. Viscoelastic properties of the gelled polymer-silicate hydrogels were measured on the samples after 24 hours from the moment of their preparation. The measurement was carried out at a constant frequency of 1 Hz within 10 min. The measuring gap was set at 2 mm. The last rheological test the polymer-silicate hydrogels were subjected to, was the creep-recovery test. Three cycles of creep-relaxation were made for each sample. 10 Pa pressure was applied during the creep stage, while relaxation stage consisted of subtracting this strength. Each stage lasted 120 s. The measuring gap was set at 2 mm. All the described measurements were performed at room temperature and repeated three times for each system.

3. Results and discussion

3.1. Polymerization kinetics

Figure 1 presents graphs of the G' and G" moduli over time and variable frequency for the R-150:ANa polymer-silicate hydrogels. From the beginning of the measurement, for each mass ratio, G' modulus has higher values than the G" modulus. As the measurement was started immediately after adding the initiators to the sample, the lack or very fast cross-over point indicates a rapid onset of gelation of the system. We can notice a decrease in the value of both moduli after 20-25 minutes on each of the graphs. After some time, these values begin to increase again, which can be called further gelation of the system. This effect can most likely be associated with the nature of the tested polymer-silicate hydrogels. When the hydrogel is practically cross-linked, the syneresis effect occurs, i.e. the polymer network shrinks, releasing a certain amount of water, which reduces the value of the moduli. However, this water is again absorbed and the value of these parameters increases again [10].Other tested hydrogels behaved similarly.

Table 3 contains values of the G' modulus in the subsequent minutes of measurement for all analyzed hydrogel systems.

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Figure 1. Dependence of G'/G" moduli over time and frequency for the R-150:ANa polymer-silicate hydrogels during polymerization

	WG		R-145		R-150		
	М	2.5			2.1		
Acrylate	Mass ratio	1:2	1:1	2:1	1:2	1:1	2:1
	Modulus		G' [Pa]			G' [Pa]	
	10 min	$14.3 \cdot 10^3$	$24.9 \cdot 10^4$	$10.8 \cdot 10^4$	$31.1 \cdot 10^4$	$12.6 \cdot 10^4$	$76 \cdot 10^3$
ANa	20 min	$12.7 \cdot 10^3$	$26.5 \cdot 10^4$	$52.5 \cdot 10^3$	$41.5 \cdot 10^4$	$77.1 \cdot 10^3$	$11.3 \cdot 10^4$
	30 min	$15.1 \cdot 10^3$	$25 \cdot 10^4$	$50.5 \cdot 10^3$	$46.3 \cdot 10^4$	$67.2 \cdot 10^3$	$12.5 \cdot 10^4$
	10 min	-	$61.3 \cdot 10^3$	$81.5 \cdot 10^4$	$37 \cdot 10^4$	$28.3 \cdot 10^3$	$12.2 \cdot 10^4$
AK	20 min		$12.6 \cdot 10^4$	$92.1 \cdot 10^4$	50.10^{4}	$20.2 \cdot 10^3$	$11.6 \cdot 10^4$
	30 min		$15.8 \cdot 10^4$	$99.2 \cdot 10^4$	$57.9 \cdot 10^4$	$41.9 \cdot 10^3$	$12.4 \cdot 10^4$
	10 min	$23.9 \cdot 10^4$	$27.2 \cdot 10^4$	$26.5 \cdot 10^4$	$39.3 \cdot 10^3$	$64.7 \cdot 10^4$	$48.8 \cdot 10^4$
AK:ANa 0.8:0.2	20 min	$29.5 \cdot 10^4$	$33.4 \cdot 10^4$	$24.1 \cdot 10^4$	$85.6 \cdot 10^3$	$81.3 \cdot 10^4$	$32.6 \cdot 10^4$
0.0.0.2	30 min	$36.1 \cdot 10^4$	$37.7 \cdot 10^4$	$21.4 \cdot 10^4$	$16.3 \cdot 10^4$	$84.6 \cdot 10^4$	$33 \cdot 10^4$
	10 min		$35.2 \cdot 10^4$	$24.8 \cdot 10^4$	$67.2 \cdot 10^3$	$19.2 \cdot 10^{3}$	$38.1 \cdot 10^4$
AK:ANa 0.5:0.5	20 min	-	$38 \cdot 10^4$	$28.3 \cdot 10^4$	$84.7 \cdot 10^3$	$18.4 \cdot 10^{3}$	$36.3 \cdot 10^4$
	30 min		$37.1 \cdot 10^4$	$30.9 \cdot 10^4$	$11.3 \cdot 10^4$	$17.7 \cdot 10^4$	$35.2 \cdot 10^4$
AK:ANa	10 min		$17.9 \cdot 10^4$		$23.4 \cdot 10^4$	$27.1 \cdot 10^4$	$44.9 \cdot 10^4$
	20 min	-	$15.1 \cdot 10^4$	-	$23.9 \cdot 10^4$	$28.5 \cdot 10^4$	$40.5 \cdot 10^4$
0.2.0.0	30 min		$13.4 \cdot 10^4$		$23.6 \cdot 10^4$	$29.1 \cdot 10^4$	$38.8 \cdot 10^4$

Table 3. Values of the G' modulus over time of the analyzed polymer-silicate hydrogel systems.

Based on the presented results, it can be seen that for some samples, the change of sodium water glass from R-150 to R-145 caused a delay in the onset of gelation of. However, change of the value of the moduli is not straightforward. For some samples it increases and for others it decreases, regardless

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of the hydrogel composition. This does not allow to unequivocal determination of the effect of the change of the water glass (silicate modulus) on the gelation rate of polymer-silicate hydrogels. In most cases, increment of the amount of silica in the sample resulted in an increase in the G' modulus value. All samples began to gel very quickly, within a few minutes. Even if a cross-over point could be observed, it was in the first seconds of the measurement. It can be seen that the samples with potassium acrylate and 0.5:0.5 of sodium-potassium acrylate were characterized by the highest degree of gelation (the highest values of the G' modulus) in most cases. The lowest values showed the samples with sodium acrylate and they started to gel at the latest.

3.2. Viscoelastic measurements

Figure 2 presents the dependence of G'/G'' moduli over time for the polymerized R-150:ANa polymersilicate hydrogels. It can be seen, due to the linear shape of the curve, that 24 hours after preparation completely polymerized hydrogels were obtained. The most elastic samples were obtained for the 1:1 mass ratio of the sodium water glass to the acrylate and the least elastic were obtained for the 2:1 system, with the highest amount of the sodium water glass. Change of sodium water glass from R-150 to R-145 resulted in decrease of the G' and G'' moduli values in most of the samples. R-145 has a larger silicate modulus, i.e. contain more silica. Such dependence could confirm that higher content of silica weaken the gel elasticity. Unfortunately, samples with 0.2:0.8 sodium-potassium acrylate showed an inverse relationship. Table 4 shows the calculated values of the phase shift angle φ (tg φ =G''/G') for all of the analyzed hydrogel samples.

The φ angle varied in different ways for different samples, so no definite conclusion can be drawn about the analyzed changes. It can only be said that the samples with the highest content of sodium water glass, i.e. 2:1, regardless of the type of used acrylate, have the least degree of elasticity, while samples with sodium acrylate are characterized by the highest degree of elasticity [11, 12].



Figure 2. Dependence of G'/G" moduli over time for the polymerized R-150:ANa hydrogels

WG		R-150			R-145	
М		2.1			2.5	
Mass ratio	1:2	1:1	2:1	1:2	1:1	2:1
ANa	11.59	6.60	26.13	19.55	10.93	32.97
AK	11.43	15.72	18.93	-	26.34	18.55
A(K:Na) 0.8:0.2	15.54	14.58	20.26	14.64	13.72	23.02
A(K:Na) 0.5:0.5	17.28	18.76	28.28	-	17.29	26.42
A(K:Na) 0.2:0.8	16.04	21.43	28.21	-	-	15.95

Table 4. Values of the phase shift angle of the tested polymer-silicate hydrogels.

3.3. Creep-recovery tests

The result of the creep-recovery test is the creep susceptibility value J [1/Pa], which, multiplied by the specific pressure, is the deformation expressed as a percentage. The obtained results are presented in the form of a graph of the deformation versus time (Figure 3). A ymax, determining the total viscoelastic deformation, was also calculated (Table 5) [13, 14].



Figure 3. Deformation of the R-150:ANa hydrogels versus time during the creep-recovery test.

Table 5. Values of the maximum deformation (ymax) of the tested silicate-polymer hydrogels.

WG		R-150			R-145	0
М		2.1			2.5	
Mass ratio	1:2	1:1	2:1	1:2	1:1	2:1
ANa	-	0.73	8.86	9.64	0.35	-
AK	4.84	3.37	7.56	-	9.98	5.46
A(K:Na) 0.8:0.2	7.43	5.01	12.03	4.05	3.46	12.10
A(K:Na) 0.5:0.5	-	4.81	-	-	4.18	8.41
A(K:Na) 0.2:0.8	0.91	24.73	28.53	-	-	-

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Figure 3 lacks a deformation curve for a 1:2 composition because negative values were obtained. This may mean that the samples were damaged during the measurement, i.e. they did not show an adequate degree of elasticity (positive values were obtained only for one sample). Analyzing the results presented in Table 5, it was noticed that in most cases samples containing higher amount of silica (2:1) showed higher maximum deformation, i.e. they were more susceptible to deformation. They were usually also characterized by a higher content of viscous character. The lowest ymax values were found for samples with sodium acrylate and with both types of sodium water glass with a 1:1 mass ratio of glass to acrylate. These results partly overlap with the measurement of viscoelastic properties, where the lowest phase shift angle was obtained for R-150: ANa samples with a 1:1 mass ratio. However, due to the fact that for a large number of samples negative deformation values were obtained, it is not possible to clearly determine the impact of the type of water glass and acrylate on the creep of gels.

4. Conclusions

Analysis of the obtained results of the rheological measurements allowed for the following conclusions:

- The best rheological results were obtained for the samples with R-150 sodium water glass, i.e. samples with the lowest value of silicate modulus and highest content of sodium oxide.
- Hydrogels with higher content of sodium water glass polymerize faster. The lower the silicate modulus is, the polymerization reaction starts faster.
- Hydrogels samples with higher polymer content show better elastic properties, i.e. value of the phase shift angle is lower.
- There is no significant dependence between the silicate modulus and the phase shift angle values.
- Hydrogels samples with sodium acrylate have the lowest susceptibility to deformation.

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