

Effect of silicate module of water glass on rheological parameters of poly(sodium acrylate)/ sodium silicate hydrogels

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Abstract. The poly(sodium acrylate)/ sodium silicate hydrogels were synthesized in the presence of sodium thiosulphate and potassium persulphate as the redox initiators and N,N'-methylene-bisacrylamide as the cross-linking monomer. 20 wt% aqueous solution of sodium acrylate was polymerized together with water glass with different silicate modules (M) from 1.74 to 2.29, in three mass ratio of the monomer solution to the water glass 2:1, 1:1 and 1:2. Such obtained hybrid composites were rheologically tested using the oscillation method. It allowed to designate the crossover point during polymerization, as well as to define the viscoelastic properties of the casted hydrogel samples one week after the reaction.

The obtained results of the oscillation measurements showed that cross-linking reaction proceeds very quickly and the lower the silicate module is, the process starts faster. After the completion of the reaction the silicate-polymer hydrogels are strongly elastic materials and the highest elasticity characterizes systems with the mass ratio 1:2, i.e. with the highest water glass content.

Keywords: silicate module, sodium water glass, oscillation rheology, silicate-polymer hydrogels, sodium polyacrylate

1. Introduction

Despite the extensive use of water glass in the industry, beginning with production of cosmetic pigments and ending with corrosion protection, this compound is not fully understood in terms of its structure and properties. Due to the fact that water glasses are not very stable systems, i.e. silicic acid undergoes facile polymerization during storage what leads to changes in its structure and composition, a few research centers in the world conduct research in this area. It is also difficult to determine the exact formula of water glass because it is a mixture of cyclic and linear silicate oligomers, which arise from cracking of Si-O-Si bonds in silica to create Si-ONa (K) groups in this place. And for example, sodium water glass, being the aqueous solution of sodium silicates, is described as $\text{Na}_2\text{O}-n\text{SiO}_2$ [1-3].

Quantity that characterizes composition of the water glass is a molar (silicate) modulus (M) which is defined as it follows (an example for sodium water glass) [4]:

$$M = \frac{X_2}{X_1} \cdot 1.032 \quad (1.1)$$

where: X_1 - sodium oxide content [%], X_2 - silica content; 1.032- conversion factor of weight units to molar units.

Depending on the molar module and other parameters such as density, viscosity etc., water



glass is classified into types. Table 1 shows characteristics of some commonly used in trade sodium water glasses.

Table 1. Characteristics of selected types of sodium water glasses [4]

Requirements	Type of sodium water glass					
	137	140	142	145	149	150
Molar module	3.2-3.4	2.9-3.1	2.6-2.8	2.4-2.6	2.8-3.0	1.9-2.1
Content of (SiO ₂ +Na ₂ O) [%] not less than	35.0	36.0	38.0	39.0	42.5	40.0
Density (20°C) [g/cm ³]	1.37-1.40	1.40-1.43	1.42-1.45	1.45-1.48	1.49-1.51	1.50-1.53
Viscosity (Pas) not less than	10	5	10	10	70	10

As it was mentioned before, structure of sodium silicates in aqueous solutions is very complicated. This is due to an atomic structure of silicon itself, which changes the coordination number from 4 to 6 (free 3d orbitals may take the extra pairs of electrons), and the presence of hydroxyl groups. Studies have shown that the colloidal nature of the sodium silicate solutions is the greater the higher the concentration and the molar module are. Thus, in solutions of sodium water glass with a module $M=2$ there are not only monosilicate groups $[H_3SiO_4]^-$, but also there are dimer silicates $[H_4Si_2O_7]^{2-}$. However, in glasses which have molar module greater than 2, revealed the presence of units containing up to 12 silicon atoms [5].

Due to the fact that water glasses are solution of high pH, above 11, polymerization of mixtures containing them causes certain problems. For example, when we want to introduce an aqueous solution of vinyl monomer such as sodium acrylate with a neutral pH to such system, acrylate precipitates from the solution and it can be only dissolved by the introduction of additional water. We also know that above $pH=7$ the polymerization rate of acrylates increases, reaching a maximum at $pH=10$, and then begins to fall in the range of $pH = 11-12$, what is explained by the decrease in the degree of polymer chain termination caused by the repulsion of polyions of the same charge [6 -10].

In the present work, due to the fact that the polymerization of vinyl monomers takes place at high temperatures and it is an exothermic process, a redox initiators system lowering the temperature of reaction was used [6,11]. As the cross-linking monomer N,N'-methylenebisacrylamide having double vinyl bond was used.

To assess the rate of polymerization and to estimate the effect of the silicate module on the rheological properties of the synthesized polymer-silicate gels method of oscillation measurement, which is based on measuring the deformation caused by sinusoidally variable stress, was used. Oscillation rheometry allows to observe of the gelling process without destroying the resulting gel network, and therefore these measurements can be used both to observe the sol gel transition as well as examination of the gelled samples [12].

Obtained results of rheological tests can be used i. a. to design the composition of polymer-silicate hydrogels used for example in the construction industry for the production of fireproof window panels or waterproofing barriers.

2. Materials and methods

2.1. Materials

As a sodium silicate aqueous solution were used sodium water glasses (WG) with the silicate modulus in the range $M=1.74-2.29$ (Table 2), purchased from the Rudniki Chemical Plant (Rudniki, Poland). Polymer filler Midafen R-102 (MR-102) came from Lubrina S.A. (Poland). Vinyl monomer solution, i.e. 20 wt% aqueous solution of sodium acrylate, was laboratory synthesized, remembering that due to

the exothermic character of the reaction, mixture temperature can not exceed 40 °C. Acrylic acid, produced by Lach-Ner (Czech Republic), was neutralizing to pH=7 with a stoichiometric volume of the 22 wt% aqueous solution of sodium hydroxide (Stanlab SJ, Poland). After that, the resulting solution was diluted to 20 wt% (20% ANa).

The polymerizing agents, i.e. the cross-linking monomer N,N'-methylenebisacrylamide (NNMBA) and system of redox initiators, potassium persulphate (KPS) and sodium thiosulphate (NTS) were delivered by Avantor Performance Materials Poland S.A. All reagents were used as supplied, without further purification.

Table 2. Characteristics of the used in test sodium water glasses

Type of the glass	Silicate module M	Density [g/cm]	pH	Na ₂ O+SiO ₂ [%]
A	1.82	1.51	12.30	39.70
A1	1.74	1.55	12.40	44.60
A2	2.20	1.47	11.90	40.70
A3	2.29	1.52	11.80	43.80

2.2. Synthesis of hydrogels

Synthesis of poly(sodium acrylate)/sodium silicate hydrogels was divided into two parts. The first part consisted of the preparation of the so-called base mixture by distributing of 5 wt%, 10 wt% and 20 wt% of Midafen R-102 (MR-102) in particular water glass (WG). Only in the case of 20 wt% of Midafen R-102 with water glass type A1 (M=1.74) base mixture wasn't prepared. Because of the high density of the used water glass this mixture was delaminated.

Table 3. Composition of the synthesized polymer silicate hydrogels

Sample symbol*	MR-102 [g]	WG [g]	20% ANa [g]	NNMBA [g]	KPS [g]	NTS [g]
2:1/5%	0.50	9.50	20.00	0.10	0.05	0.05
2:1/10%	1.00	9.00				
2:1/20%	2.00	8.00				
1:1/5%	0.75	14.25	15.00			
1:1/10%	1.50	13.50				
1:1/20%	3.00	12.00				
1:2/5%	1.00	19.00	10.00			
1:2/10%	2.00	18.00				
1:2/20%	4.00	16.00				

*Sample symbol: for e.g. 1:1/5% - 1:1 means a mass ratio of 20 wt% aqueous solution of sodium acrylate to a base mixture, which consists of sodium water glass A1 and a polymer filler Midafen R-102 (5-20%)

The second step concerning the free radical polymerization of base mixture together with 20 wt% aqueous solution of sodium acrylate (20% ANa) at a mass ratio of 2:1, 1:1 and 1:2 of vinyl monomer solution to the base mixture. After mixing these two main components it was noticed that the higher the silicate module was, the amount of water needed to dissolve the precipitated sodium acrylate was higher (from 1 to 5 ml). The cross-linking monomer (NNMBA) and system of redox initiators

(KPS/NTS) were added to the mixture in an amount of 0.3 wt% to the sample weight (Table 3).

2.3. Rheological measurements

The oscillation measurements, i.e. frequency sweep standard tests, were performed with a Physica MCR-301 Anton Paar rheometer at low shear rates in the range of angular frequencies $500-0.05\text{ s}^{-1}$ and in room temperature. As a measuring system was used a parallelplate system where the upper plate (PP50) has a 50 mm diameter.

During the cross-linking reaction, where the sample was immediately transferred to the measuring system after preparation, the gap between plates was set at a distance of 0.10 mm, while during the same oscillation test of the cast samples (7 days after preparation) the gap was set at a distance of 1 mm.

3. Results and discussion

3.1. Frequency sweep standard test during cross-linking process

Figures 1 and 2 show the dependence of G' and G'' moduli as a function of angular frequency during cross-linking process for samples based on sodium water glass (A1) with molar module $M=1.74$. Because the measurement time was only about 30 minutes, it was hard to determine the plateau region from which we can read the exact values of G' and G'' moduli. So, to describe the polymer-silicate system during the cross-linking process, we use cross-over points (marked on the graph with colored arrows).

Cross-over point, in other words gel point, the moment at which the phase transition occurs to a viscoelastic solid, occurs quite fast. The fastest for the mass ratio 2:1, then 1:1 and 1:2 at the end. Confirmation of these observation are the values of angular frequency included in Table 4, where we present results for other polymer-silicate samples during cross-linking process.

Analyzing these results, it should be remember that water glass designated as A is not a pure sodium silicate solution, but it contains small amounts of aluminum. Also here we can see that cross-linking process starts faster, if we have more monomer in the solution. Presumably at higher pH, i.e. with higher content of sodium silicate solution, cross-linking monomer and redox initiators decompose more rapidly. Second conclusion concerns the molar module- the higher the content of sodium silicate the process starts later.

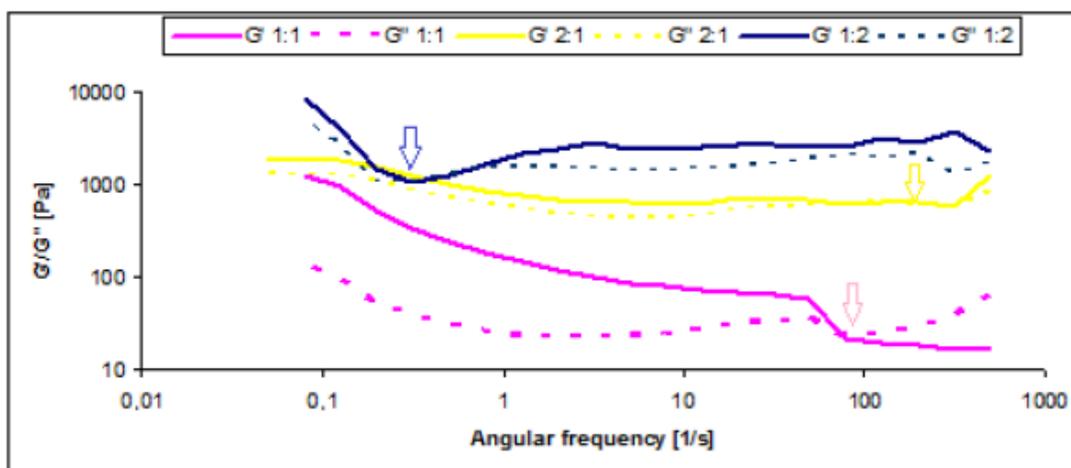


Figure 1. G' and G'' moduli as a function of angular frequency during cross-linking process for samples based an A1 sodium water glass with 5% of polymer filler

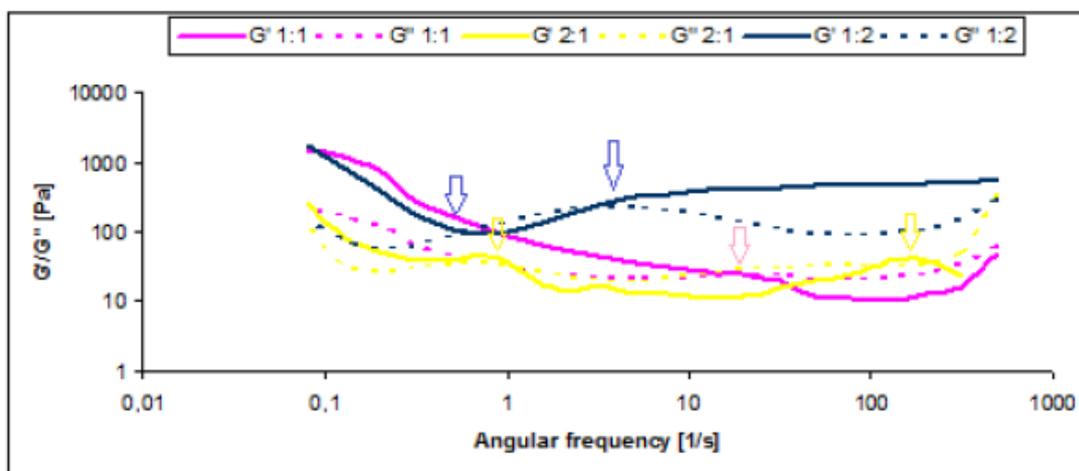


Figure 2. G' and G'' moduli as a function of angular frequency during cross-linking process for samples based on A1 sodium water glass with 10% of polymer filler

Table 4. Values of the cross-over angular frequencies for the tested hydrogel samples during cross-linking process

Type of water glass		A	A1	A2	A3
MR-102 [wt%]	Mass ratio	« [rad/s]			
5	2:1	118.65	360.61	-	287.60
	1:1	105.53	176.29	326.41	4.21
	1:2	0.87	73.19	182.10	2.47
10	2:1	108.21	207.51	216.16	140.53
	1:1	15.48	19.24	65.52	12.30
	1:2	-	2.76	6.68	-
20	2:1	66.52	-	33.89	297.57
	1:1	1.65	-	29.33	10.32
	1:2	-	-	10.41	0.56

3.2. Frequency sweep standard test- ageing tests

The second frequency sweep standard test was carried out to check the influence of the mass ratio of the poly(sodium acrylate) to the base mixture on the viscoelastic properties of the tested samples after the cross-linking reaction. As it is shown in Figures 3 and 4, the storage (elasticity) modulus G' and the loss (viscous) modulus G'' strongly depend on the sample composition and G' is higher than G'' which means that we obtain more elastic than viscous hydrogels. Comparing the values of G' and G'' with the polymer content, it was found that less poly(sodium acrylate) was present, the values of both moduli were higher.

To assess the viscoelastic properties of the cast samples we calculated phase shift angle, i.e. tangent of the quotient of the G'' to G' (Table 5). It was found that for the obtained polymer-silicate hydrogels phase angle is low, below 40° , what indicates that we got highly elastic hydrogels (90° denotes a totally viscous substance and 0° is related to a completely elastic systems) and the most elastic are samples with the higher content of water glass. Comparing the phase angle in terms of molar module we see that this value is the lowest for the highest module 2.29 (A3), i.e. for the water glass with the highest content of sodium silicate.

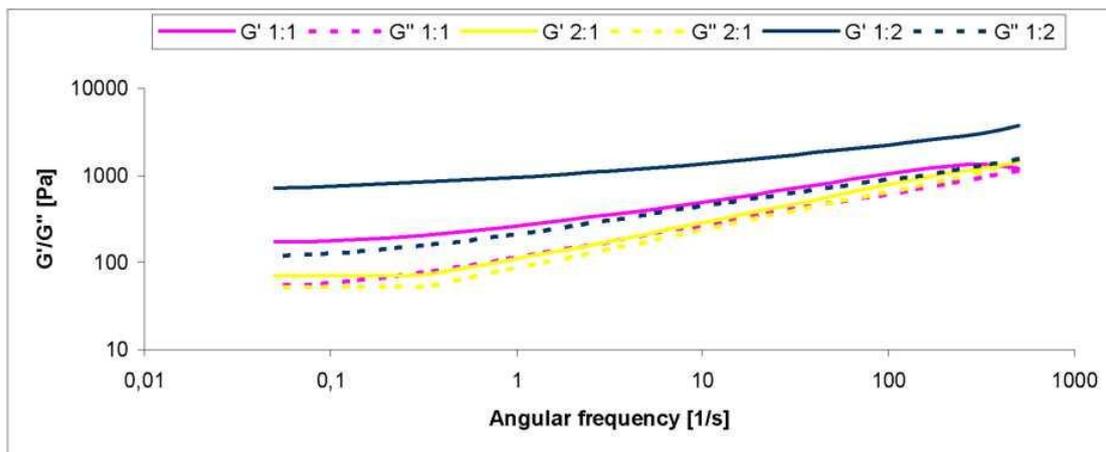


Figure 3. G' and G'' modules as a function of angular frequency for cast samples based on A1 sodium water glass with 5 % of polymer filler

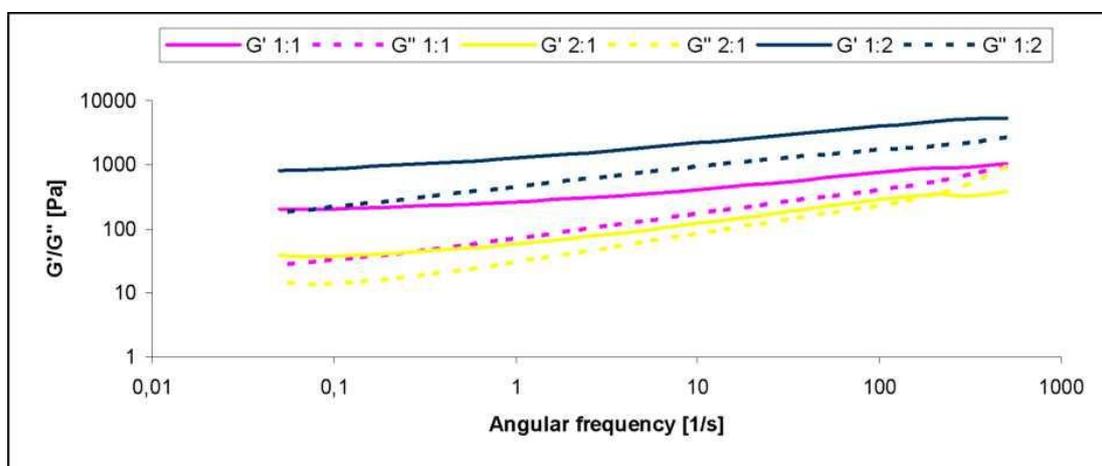


Figure 4. G' and G'' modules as a function of angular frequency for cast samples based on A1 sodium water glass with 10% of polymer filler

Table 5. Values of phase shift angle for cast samples of poly(sodium acrylate)/ sodium silicate hydrogel

Type of glass		A	A1	A2	A3
MR-102 [wt%]	Mass ratio	O n			
5	2:1	-	36.87	-	-
	1:1	31.96	18.83	30.41	15.91
	1:2	24.84	9.98	28.90	-
10	2:1	18.11	21.80	35.22	-
	1:1	11.25	9.20	11.80	38.87
	1:2	5.48	13.60	9.31	22.19
20	2:1	29.60	-	41.70	14.73
	1:1	23.80	-	31.80	10.26
	1:2	13.33	-	12.24	8.87

4. Conclusion

In the present work the oscillation constants of the polymer-silicate system have been investigated. It was noticed that the mass ratio and type of the used sodium water glass has a big influence on the G'

and G'' values and controlling these two variables more viscous or more elastic gels can be obtained:

- the lower the silicate module is, the amount of water needed to dissolve the precipitated sodium acrylate is smaller;
- the lower the silicate module is, the cross-linking reaction starts faster;
- the obtained polymer-silicate hydrogels are relatively elastic materials; the higher the water glass content the phase shift angle is smaller, i.e. the most elastic hydrogels were obtained for the mass ratio of the sodium acrylate water solution to the base mixture 1:2. There was no dependence between the silicate module value and the phase shift angle.

Summing up, obtained results of rheological tests can be used i. a. to design the composition of polymer-silicate hydrogels used for example in the construction industry for the production of fireproof window panels or waterproofing barriers.

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