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Rheological properties of polymer basis for hydrogel dressings of biomedical application

This research was conducted in order to develop the technology of obtaining the new hydrogel dressings based on polyvinylpyrrolidone and agar-agar for treatment burns and wounds. Rheological parameters of polyvinylpyrrolidone and agar-agar solutions were studied with the help of on rotational viscometer Rheotest RV-2.1. The effect of different factors (concentration, temperature, thixotropy) on the rheological properties of polyvinylpyrrolidone and agar-agar solutions was investigated. the main regularities of intermolecular interaction processes that influence on structure formation in polyvinylpyrrolidone and agar-agar concentrative solutions were determined.

Keywords: Polyvinylpyrrolidone, agar-agar, hydrogel, dynamic viscosity, intermolecular interaction.

Introduction

The development of science and technology is leading to more widespread adoption in medicine of synthetic and natural highmolecular polymer compounds. Among the polymers used in medicine are synthetic and natural materials, bioinert (not degradable in biological fluids) and breakable (bioresorbable) polymers, highly crystalline and rubbery thermoplastic elastomers [1]. Properties of hydrogels (swelling, mechanical properties, degradability) are important to determine their application. Hydrogels due to the high water content have low mechanical properties. A common way to control the mechanical properties of the hydrogels to change polymer cross-linking density. Mechanical properties of the hydrogel depend on polymerization conditions during the formation of network. In turn, mechanical properties of the hydrogel characterize its swelling.

The results of scientific researches [2-10], conducted over the past several decades on Department of Chemistry and Technology of Organic Substances, Natural Compounds and Polymers in Al-Farabi Kazakh National University, allowed to create new hydrogel dressings based on polyvinylpyrrolidone and agar-agar for treatment burns and wounds. Materials based on polyvinylpyrrolidone (PVP) are recommended to cover the burns and other wounds oozing. Antimicrobial agents can be added to transparent elastic material, which prevents the wound infection.

The goal of the research is the study of rheological parameters of polyvinylpyrrolidone and agar-agar solutions; the effect of different factors (concentration, temperature, thixotropy) on their rheological properties and the determination of main regularities of intermolecular interaction processes that influence on structure formation in polyvinylpyrrolidone and agar-agar concentrative solutions.

Materials and methods

Characterization of the raw materials

Polyvinylpyrrolidone (PVP) “Kollidon 90F”, Mw = 1000000-1500000, CAS №9003-39-08 («BASF group», Germany) was used without additional purification.

Bacteriological agar-agar, CAS №9002-18-0 ("Sigma Aldrich", USA) was used without additional purification.

Preparation of solutions

In research different concentrations of PVP and agar-agar solutions were prepared: [PVP] = 5; 10;

20; 30; 40 mas. %; [Agar-agar] = 0.5; 1; 3; 5; 7 mas.%.

Polymer solutions in water were prepared in a volumetric flask of 500 ml using an ultrasonic bath Bandelin electronic DT 103H.

Physico-chemical methods of research

The study of rheological properties was carried out on thermostated rotational viscometer Rheotest RV-2.1 using "cylinder in cylinder" system. S1 cylindrical measuring device was used that allows to measure dynamic viscosity in range 1÷100000 Pa·s.

Methods for data analysis

Calculation of dynamic viscosity:

$$\eta = \tau/D\cdot 100,$$

where: η – dynamic viscosity, Pa·s; τ – shear stress, Pa; D – shear rate, s-1.

Calculation of shear stress:

$$\tau = z\cdot\alpha,$$

where: z – cylinder constant, Pa/scale units;α – instrument readings, scale units.

The values of the shear rate D and constant cylinder z are tabular data [11].

The results are presented in the form of dependence curves of the dynamic viscosity η from the shear stress τ and of the shear rate D from the shear stress τ.

Results and discussions

Based on retrieved data the main rheological curves for PVP and AA solutions were obtained: flow curve (dependence of shear rate D from shear stress τ) and viscosity curve (dependence of dynamic viscosity η from shear stress τ).

Figures 1, 2 and figures 3, 4 present main rheological properties of PVP and AA solutions (dependence of shear rate D from shear stress τ and dependence of dynamic viscosity η from shear stress τ).

Figure 1 shows the dependence of shear rate D from shear stress τ of PVP solutions of different concentrations ([PVP] = 5; 10; 20; 30; 40 mas. %) at 25°C.

Figure 2 shows the dependence of shear rate D from shear stress τ of agar-agar solution of concentration [AA] = 1 mas. % at 25°C.

The data presented on Figures 1, 2 shows that the curves of shear rate versus shear stress at various concentrations are clearly nonlinear. Nonlinearity of the system is expressed in the absence of a direct proportionality between shear stress and strain produced.

For all the curves the deformation occurs not immediately after application of shear forces but after a certain limit (≈ 5-9 Pa). The further course of the curve indicates the break of bonds between particles and, accordingly, the deformation increases stronger than the applied voltage. Hence

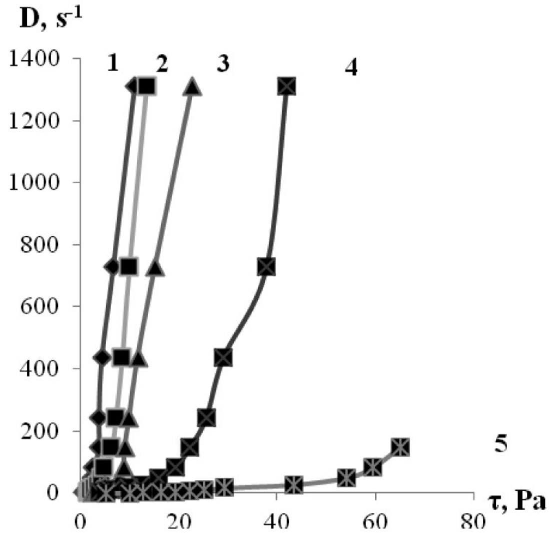

Figure 1 – Dependence of shear rate D from shear stress τ of PVP solutions, 25° C.
Note: [PVP] = 5 (1); 10 (2); 20 (3); 30 (4); 40 (5) mas.%

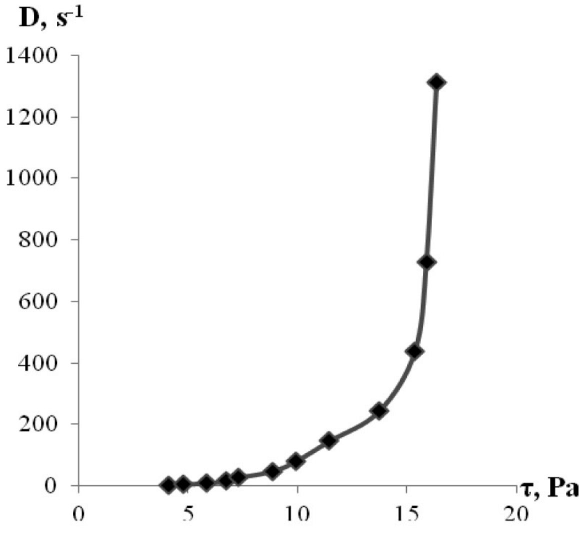

Figure 2 – Dependence of shear rate D from shear stress τ of agar-agar solution, 25°C.
Note: [Agar-agar] = 1 mas. %

it can be seen that the PVP and AA solutions are not Newtonian fluids, i.e. more pseudoplastic liquids.

Figure 3 shows the dependence of dynamic viscosity η from shear stress τ of PVP solutions of different concentrations ([PVP] = 5; 10; 20; 30; 40 mas. %) at 25^o C.

Figure 4 shows the dependence of dynamic viscosity η from shear stress τ of agar-agar solution of concentration [AA] = 1 mas. % at 25^o C.

As seen from Figures 3, 4 an increasing the shear stress leads to decreasing the dynamic viscosity.

Tangles of high molecular weight are elastic (large tangle size contributes to its greater tensile strength under the influence of the velocity gradient). Elastic tangles now moved as a whole in the molten medium with smaller molecules.

Turning off" from the segmental flow of tangles (high molecular weight) reduces the cost of energy, decreases resistance to the movement of flow, the viscosity decreases. A similar process occurs with tangles of smaller size, where the shear stress increases. With the increase in shear stress all the other factions in turn cease to participate in the segmental flow. There is a gradual decrease in viscosity with increasing τ.

As seen from the graphs of Figures 5, 6 dynamic viscosity of PVP and AA solutions depends on shear stress and changes in the range of 1 ÷ 140 Pa·s. The sharp change of the dynamic viscosity is in the range of 10 ÷ 50 Pa · s. The maximum value of dynamic viscosity at the same shear rate in the range 20 ÷ 140 Pa·s.

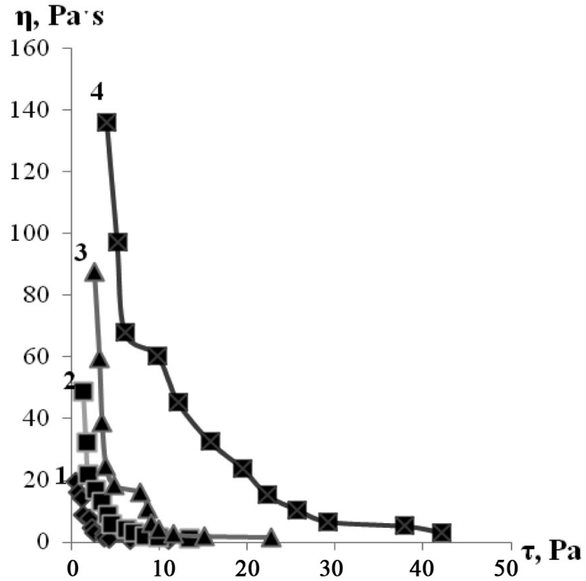

Figure 3 – Dependence of dynamic viscosity η from shear stress τ of PVP solutions, 25^o C.
Note: [PVP] = 5 (1); 10 (2); 20 (3); 30 (4) mas.%

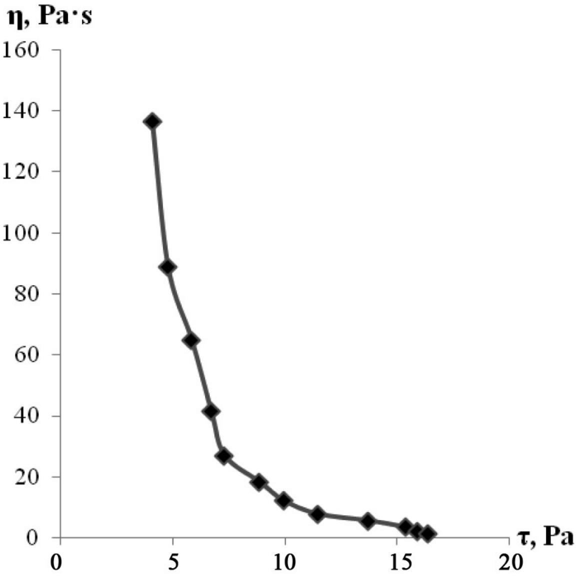

Figure 4 – Dependence of dynamic viscosity η from shear stress τ of agar-agar solution, 25^{o}C.
Note: [Agar-agar] = 1 mas. %

The main characteristics and the main changes of viscosity curves of PVP and AA solutions of different concentrations can be seen from the Table 1.

The value of the dynamic viscosity allows to estimate the intensity of the processes of structure formation in the material. The dynamic viscosity is related to the internal friction forces, and is characterized as the ratio of the force causing a shift to the shear caused by this. For structured systems the interaction of aggregate particles with each other is characterized, thus the formation of frame between aggregates of particles by hydrogen bonds and van der Waals forces is occurred. The increase of deformation leads to the destruction of the carcass fugitive. At the same time simultaneously the processes of destruction of units, as well as the processes of association take place. With increasing shear stress mainly structural failure occurs, as well as the particle orientation in direction of the deformation; accordingly the interaction between them decreases and distortion increases. As can be

Table 1 – The main characteristics of viscosity curves of PVP solutions.

	5 mas. % of PVP	10 mas. % of PVP	20 mas. % of PVP	30 mas. % of PVP	1 mas. % of AA
Range of viscosity	1-20 Pa·s	1-50 Pa·s	1-90 Pa·s	1-140 Pa·s	1-140 Pa·s
Sharp change of viscosity	3-4 Pa·s	5-6 Pa·s	8-10 Pa·s	20-60 Pa·s	10-40 Pa·s
Maximum value of viscosity	20 Pa·s	50 Pa·s	90 Pa·s	140 Pa·s	140 Pa·s

seen from the data presented in Figures 3, 4, the dynamic viscosity decreases with increasing strain, while undergoing a certain section breaks.

It is known [12] that when the system is subjected to shear, units with individual macromolecules are destroyed. The effective viscosity decreases with time, when the shear rate is constant. Structural failure of thixotropic fluids occurs under these conditions, a measurable time. When removing the shear stress again there is a thixotropic structure of the material. Upon standing solutions macromolecule can aggregate again (which happens in practice), the apparent viscosity of the system increases. As is well known [26], depending on the structure of the existing system such reversion time may vary from a few seconds to several days. In this regard thixotropic properties of hydrogel were studied, i.e. the ability to recover its structure, as well as the time needed for this recovery.

Figure 5 shows the thixotropic properties of PVP solutions of different concentrations.

Dynamic equilibrium decay – restoration of the grid occurs in a flow for all values of τ. The equilibrium in the flow is provided by the thermal motion (thermo fluctuations) and shear stress sets the direction and speed of moving segments.

The appearance of a maximum on the curve «η – t» indicates thixotropy, thixotropic properties of the solution. The phenomenon is reversible: if the engine is switched off and the melt entirely is relaxed, repetitive strain at the same rate will give the same results.

The main differences of agar-agar solutions from polyvinylpyrrolidone solutions is the fact that agar-agar solutions do not have thixotropic properties. It can be explained by structure of agar-agar macromolecules. Agar-agar solutions have such property as to make a physical gel from concentrative solutions. And also there are many functional groups in agar-agar structure, especially –OH groups, and that’s why the hydrogen bonding in agar-agar solutions is much stronger than in PVP solutions. The relaxation time can be about several seconds.

On the basis of the data obtained (Fig. 5) it can be assumed for the restoration of the original structure of the polymer material after 5-10 days. The observed phenomena can be explained by the fact that with increasing shear stress is a gradual destruction of the supramolecular structure of associates of the order, which will eventually be restored under the influence of hydrogen bonding and intermolecular forces (in particular, van der Waals forces).

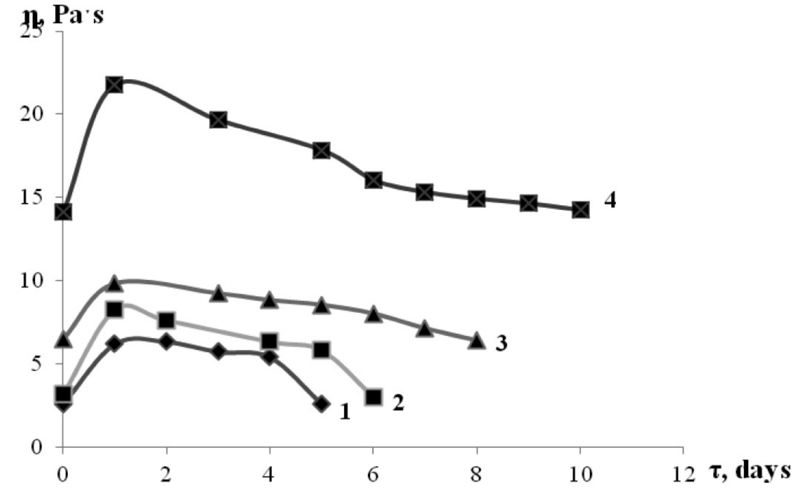

Figure 5 – Thixotropic properties of PVP solutions: dependence of dynamic viscosity η from time τ, 25^{o}C.
Note: [PVP] = 5 (1); 10 (2); 20 (3); 30 (4) mas.%

The relaxation time data can be seen from Table 2.

Table 2 – The relaxation time of PVP solutions.

The concentration of PVP solutions	The relaxation time
5 mas. % of PVP	5 days
10 mas. % of PVP	6 days
20 mas. % of PVP	8 days
30 mas. % of PVP	10 days

Macromolecules contact with each other to form a network of mobile links. Nodes links are characterized by some time of life that is reflected in the corresponding relaxation times. If the deformation is slower than the relaxation times of these, the chain moves the macromolecule "unaware" of these components – chain slip over each other, this means that the polymer flows. If the deformation is quite fast compared to the relaxation times, it is not enough time for the decay of nodes.

Normal stresses always reflect dimensional structural elements in the reaction medium at the current voltage is applied. Thus, deformation of the resin body inevitably leads to a change in conformation of macromolecules. This process – deformation or relaxation – due to statistical reasons inevitably is three-dimensional. Therefore, it would seem one-dimensional macroscopic shear deformation leads to a three-dimensional response to the micro-level.

In summary, these studies revealed the relaxation time of PVP solutions, which was approximately 5-10 days. Evidence of this is the identity of the first and last point on the curves in Figure 5.

Influence on the course of the material flow can have a concentration of the solution. In this case it is appropriate to speak of a ratio of the solid and liquid phases of solution, i.e. its concentration. The increase the moisture content in the hydrogel leads to the change of rheological properties of the test the polymeric material, as it is sometimes rheological parameters are most sensitive to changes in the structure parameters of polymers. In this regard, it considers the influence of concentration on the rheological characteristics of the sample (Figures 6, 7).

The choice of such high temperatures in the research of concentration effect to rheological parameters of agar-agar solutions is due to the specific properties of agar-agar concentrative solutions. According to literature, agar-agar is watersoluble only at high temperatures 70 and 80 oC. And the decreasing the temperature agar-agar solution becomes a physical gel and looks like a solid film. Such solid film at room temperature does not allow making some rheological investigations.

As seen from the Figures 8, 9, the increasing of the concentration of PVP and AA solutions

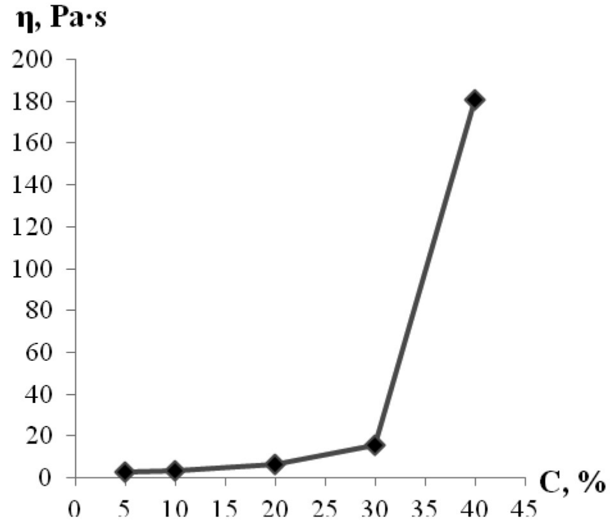

Figure 6 – Dependence of dynamic viscosity η from concentration C, 25^{o} C.
Note: [PVP] = 5, 10, 20, 30, 40 mas.%

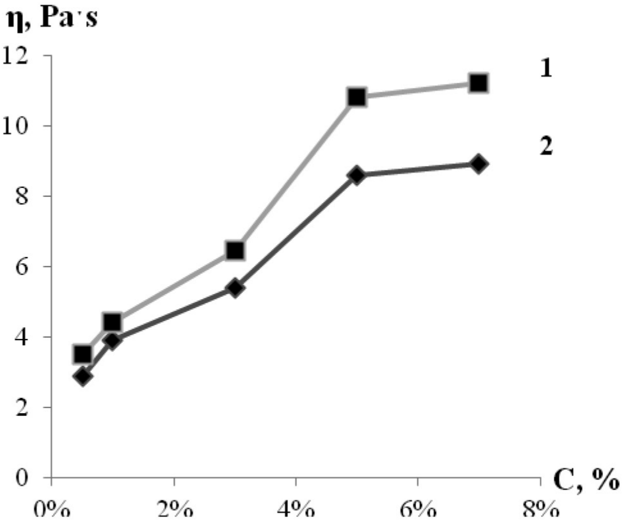

Figure 7 – Dependence of dynamic viscosity η from concentration C of agar-agar solutions.
Note: T = 70 (1); 80 (2) ^{o}C

increases the dynamic viscosity, especially it can be noticed at concentration of PVP solution [PVP] = 40 mas.% (the increase of dynamic viscosity from 15 Pa·s for [PVP] = 30 mas. % to 180 for [PVP] = 40 mas.%) and at concentrations of AA solutions [AA] = 3 mas. % and [AA] = 5 mas. % (the increase of dynamic viscosity from 4 Pa·s for [AA] = 1 mas. % to 5 Pa·s for [AA] = 3 mas.% and to 9 Pa·s for [AA] = 5 mas.%).

Such increasing in viscosity while increasing the concentration can be explained by structure formation of polymer solutions. With increasing the concentration the number of segments and macromolecules in solution increases. The structure formation becomes stronger, and the deformation must be higher to break intermacromolecular bonds.

There is another explanation of increasing the viscosity with the increasing the concentration of polymer solution. Macromolecules consist of segments, and the more segments there are, the more flexible the macromolecule is. The flow of polymer depends on the moving of segments. If there are many segments connected with each other in one big macromolecule, then moving of these segments becomes difficult. That's why the flow becomes slower that leads to the increasing of viscosity of polymer solutions.

Polymer processing is often based on molding products (semi-finished) when moving through the channel, clearance, etc. or by filling out a form feed into it melt through the channel. This process requires sometime high temperatures. And temperature is also one of the important factors that effects to the rheological properties of polymer solutions and polymer materials. That's why the effect of temperature on rheological properties of polyvinylpyrrolidone and agar-agar solutions was investigated.

Figures 8, 9 show the dependence of dynamic viscosity η from temperature T of PVP and AA solutions.

The range of temperatures for investigation the rheological properties of PVP solutions was 20°C, 30°C, 40°C, 50°C.

The range of temperatures for investigation the rheological properties of AA solutions was 20°C, 30°C, 40°C, 50°C, 55°C, 60°C, 70°C, 80°C. The concentrations of agar-agar solutions were [AA] = 0.5 and 1 mas.%. More concentrative solutions of agar-agar did not allow measuring the viscosity below 70°C because of its physical state (below this temperature concentrative agar-agar solutions become physical gels that look like solid films).

As seen from Figure 8, the temperature effects only on PVP solution with concentration of [PVP] = 30 mas.%. The effect of temperature is shown to accelerate the Brownian motion. Destroyed by the applied strain intermolecular bonds have time to recover under the fast Brownian motion. At

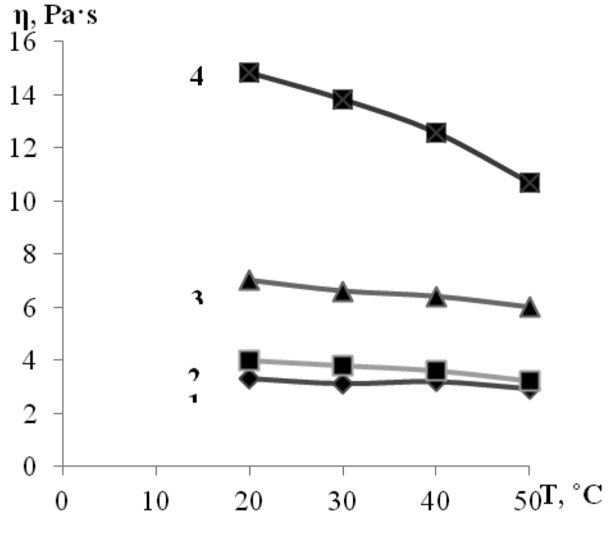

Figure 8 – Dependence of dynamic viscosity η from temperature T of PVP solutions.
Note: [PVP] = 5 (1); 10 (2); 20 (3); 30 (4) mas.%

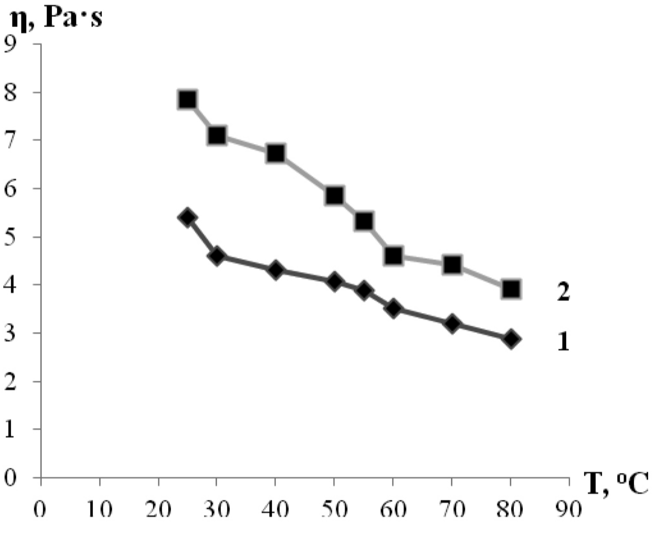

Figure 9 – Dependence of dynamic viscosity η from temperature T of agar-agar solutions.
Note: [Agar-agar] = 0,5 (1); 1 (2) mas.%

low concentrations bonds are restored, and there is no flow. Therefore, the dynamic viscosity is not changing. But at high concentrations, especially at [PVP] = 30 mas.% and more, the number of segments and macromolecules is increased, the number of bonds is also increased, and broken bonds do not have time to recover under the fast Brownian motion. The structure is deforming, the flow appears, that's why the dynamic viscosity is decreasing with the temperature increasing.

The same picture can be observed on Figure 9 for AA solutions. The main difference between PVP and AA solutions is that temperature effects on viscosity of AA solutions even at low concentrations.

The effect of temperature on rheological properties of agar-agar solutions is deeper than on rheological properties of polyvinylpyrrolidone solutions.

Thus, these studies will help in the creation of new extremely efficient hydrogel dressing on the basis of polyvinylpyrrolidone and agar-agar, which will also contain natural and herbal medicines for the treatment of burns and wounds.

Conclusion

The rheological properties of polyvinylpyrrolidone and agar-agar solutions were investigated. The effect of different factors (concentration, temperature, thixotropy) were studied. The main regularities of intermolecular interaction processes that influence on structure formation in polyvinylpyrrolidone and agar-agar concentrative solutions were determined.

1 The fact that the polyvinylpyrrolidone and agar-agar solutions are not Newtonian fluids, i.e. more pseudoplastic liquids.

2 An increasing the shear stress leads to decreasing the dynamic viscosity of polyvinylpyrrolidone and agar-agar solutions.

3 The studies of the relaxation time of polyvinylpyrrolidone solutions were carried out, which was approximately 5-10 days. Agar-agar solutions do not have thixotropic properties.

4 The increasing of the concentration of polyvinylpyrrolidone and agar-agar solutions increases the dynamic viscosity, especially it can be noticed at concentration of polyvinylpyrrolidone solution [PVP] = 40 mas.% and at concentrations of agar-agar solutions [AA] = 3 mas. % and [AA] = 5 mas. %.

5 The dynamic viscosity of polyvinylpyrrolidone and agar-agar solutions is decreasing with the temperature increasing.

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