

POLYACRYLAMIDE'S RHEOLOGICAL AND PHYSICOCHEMICAL PROPERTIES: ANALYSIS AND APPLICATIONS

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This study presents an in-depth rheological characterization of polyacrylamide polymers produced locally, employing the Anton Paar MCR 92 (Modular Compact Rheometer). The polymer samples were systematically analyzed to understand their response to various external stimuli. Using infrared spectroscopy, the composition of the polymer was meticulously verified, ensuring a robust assessment of its molecular structure and chemical stability under different environmental conditions. Our findings elucidate the significant potential of polyacrylamide in diverse industrial applications, attributable to its adaptable viscoelastic properties and chemical resilience. The implications of this research are profound, suggesting enhanced utility of polyacrylamide in fields requiring precise material behavior modulation under dynamic conditions.

Keywords: Polyacrylamide; Anton Paar MCR 92 (Modular Compact Rheometer); Rheology; Gel; Hidrogel; IR spectroscopy

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INTRODUCTION

Polymer materials, owing to their unique molecular structures and substantial sizes, are extensively utilized across various sectors of industry and technology, including construction, pharmaceuticals, and the oil and gas industries [1, 2]. For instance, these materials are employed in coatings, stabilization elements, and water retention systems, where their structural properties and characteristics play a crucial role in solving industry-specific challenges. Research indicates that polymers, particularly macromolecular compounds like polyacrylamide, are capable of participating in complex chemical and physical processes due to their high viscosity and durability. These properties ensure polymers' effective application across diverse environmental conditions [1, 4].

In the oil and gas sectors, the ability to control the cohesiveness of polyacrylamide is critically important for enhancing the efficiency of oil flow. This polymer optimizes the viscosity of liquids, thereby facilitating more effective extraction of oil from subterranean sources. Additionally, in water purification systems, polyacrylamide plays a pivotal role in the effective separation of toxic substances, which is essential for maintaining ecological stability [2, 3].

In the manufacture of pharmaceuticals, polyacrylamide plays a critical role in stabilizing drugs and controlling their dispersal, which extends the effectiveness and duration of the medications [5]. These studies and scientific discoveries delve deeper into the novel properties and practical applications of polymers, driving forward new advancements in the scientific community and the field of technology. The science and applications of polymers are becoming one of the most crucial topics in materials science, serving as a pivotal factor in the development of modern technologies [3, 5].

Rheometry is a scientific method focused on studying the flow and deformation properties of materials. This field provides information about the internal structure of materials by studying their response to flow and deformation, which is essential for understanding and predicting the mechanical behavior of materials [1-3]. Materials, particularly liquids and solids, provide extensive information about their compositional characteristics through rheometric analysis. This information, obtained through parameters such as viscosity and flow capabilities, is typically determined using specialized rheometers [2-5]. This process, known as rheotesting, allows for a precise understanding of how materials respond to dynamic and static loads. This scientific approach opens new avenues for understanding materials and their practical applications, playing a fundamental role in advancing research and developments in materials science. Rheometry creates a solid scientific foundation for accurately and reliably analyzing the physical and mechanical properties of materials [3,4,9].

X-ray analysis, especially X-ray diffraction (XRD), is another crucial method that determines the interatomic or interionic structure of crystalline and amorphous substances. This analysis provides data about the phase composition and lattice dimensions of materials. XRD data are extensively used in materials science, mineralogy, and metallurgy because this method allows for an in-depth study of the microstructural properties of materials [6, 11]. Thus, information obtained from infrared spectroscopy and X-ray analysis deeply enhances our understanding of the chemical and physical structures of materials. These analyses play an important role in defining the properties of materials and the potential applications in which they can be used, thereby laying the groundwork for further research and scientific developments [12].

EXPERIMENTAL

Materials

Polyacrylamide (PAA). Polyacrylamide is an odorless, amorphous solid with a white-yellowish color, the molecular weight of which is 10^4 – 10^7 (depending on the conditions of preparation). The density of polyacrylamide at room temperature (295–297 K) is about 1.302 g/cm^3 . The decomposition temperature is about 463 K. Polyacrylamide is a polyelectrolyte with hygroscopic properties, harmless, and forms a soft gel when dissolved in water [4, 5, 11].

Polyacrylamide (PAA) is a polyelectrolyte synthesized through the polymerization of acrylamide, which contains nitrogen, resulting in a structure that is linearly branched. This compound is produced at the Navoi Chemical Plant and complies with the standard TSh 6.1-00203849-64:1997. Polyacrylamide appears as an amorphous solid, typically white to yellowish, and is odorless. It exhibits a molecular weight of approximately $10^4 \times 10^7$, although this can vary based on synthesis conditions. At standard room temperature (around 295–297 K), its density is recorded at 1.302 g/cm^3 . Polyacrylamide decomposes at a temperature of about 463 K. Due to its hygroscopic nature, polyacrylamide is harmless and capable of forming a soft gel upon dissolution in water, leveraging its polyelectrolyte properties [3–5, 8, 12].

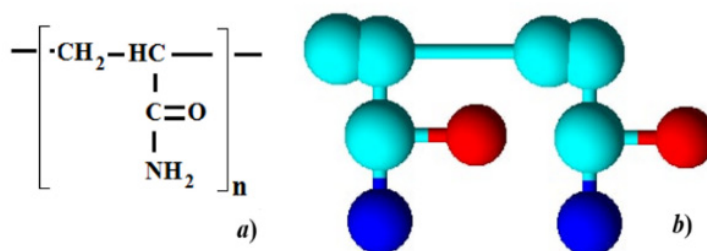


Figure 1. Chemical formula (a) and model structure of PAA (b) [4, 5]

FTIR. The structure of the obtained products was determined using IR spectroscopy and electron microscopy. IR spectra in the range 400 – 4000 cm^{-1} were recorded on “NIKOLET Magna-560 IR” and “Specord-75IR” spectrophotometers (Carl Zeiss, GDR). The samples for IR spectroscopy were prepared in the form of pellets with KBr, films on a KRS-5 plate, and films 8–12 μm thick. Films on a KRS-5 plate were obtained by evaporation of the solvent (water) at room temperature (295–297 K).

XRD. The device used for X-ray diffraction analysis is an X-ray diffractometer, which operates using X-rays emitted from a copper (Cu) source. It functions at 40 kV voltage and a current of 30 mA, capable of rotating samples within an angular range of 4° to 80° . The sample rotation speed is set at 2° per minute, ensuring accurate and reproducible measurements. The X-rays undergo diffraction within the crystal lattice, adhering to the laws of X-ray diffraction.

$$n\lambda = 2d \sin \varphi \quad (1)$$

Rheometer. Rheological studies were conducted using the Anton Paar MCR 92 (Modular Compact Rheometer), a device noted for its modernity and high sensitivity. The MCR 92 model can operate continuously for less than one day, generating rotational and oscillatory torques ranging from 1 to 125 mNm. This rheometer’s angular velocity ranges from 10^{-4} to 157 rad/s, and its angular frequency spans from 10^{-4} to 628 rad/s. The rotation speed (CSS/CSR) can be adjusted from 0.001 to 1500 rpm. The device can operate within a temperature range of -50°C to $+400^\circ\text{C}$. During the sample examination, relatively flat and slightly conical plates were used. Throughout the rheological tests, the sample temperature was maintained at a constant $25 \pm 0.5^\circ\text{C}$, enhancing the reliability and repeatability of the experimental results. These specifications highlight the device’s high precision and versatility, facilitating the accurate and effective study of the rheological properties of various materials.

Sample Preparation. The research sample of polyacrylamide was prepared under controlled conditions at room temperature (25°C). Due to the slow dissolution rate of polyacrylamide in water and to ensure thorough mixing, the 8% concentration of the sample was fully dissolved using a specialized dispenser, facilitating uniform consistency, $\text{pH} = 7.2$.

RESULTS AND DISCUSSION

The average molecular weight of polyacrylamide has been determined to be approximately $3.2 \cdot 10^6 \text{ g/mol}$ using an Ubbelohde viscometer in an aqueous medium at 25°C . Furthermore, the dynamic viscosity was quantitatively analyzed as a function of concentration employing the Huggins equation.

Infrared spectroscopy and X-ray fluorescence analyses are also important methods for material analysis. Infrared spectroscopy (IR spectroscopy) is used to study the chemical composition of materials; this method examines the vibrational characteristics of bonds within molecules, thereby identifying the types of chemical bonds between the atoms in the molecules. Through this technique, it is possible to understand the molecular structure of polymers, organic compounds, and other complex materials [5, 7, 9]. An IR spectroscopic image of polyacrylamide polymer is presented below (Fig. 2). The results obtained in the infrared region clearly show all the main bonds present in the structure of the polyacrylamide polymer.

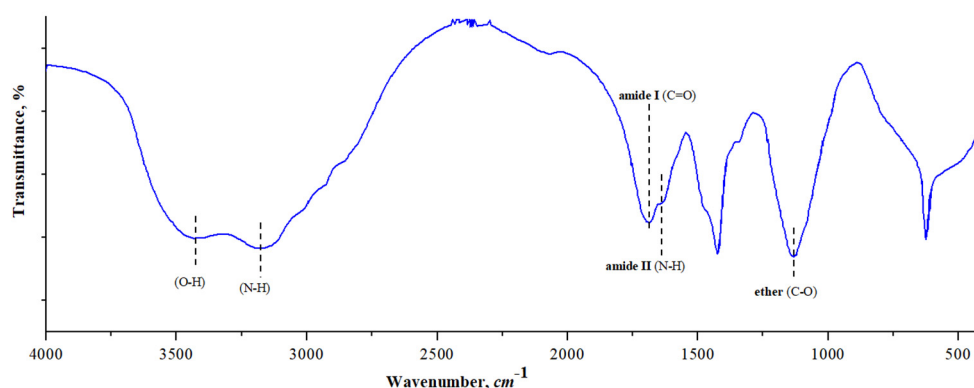


Figure 2. Infrared spectroscopic imaging of polyacrylamide polymer.

Polymers are macromolecular compounds that, while exhibiting amorphous characteristics in their dry state, also contain crystalline regions within their structure. The presence of these crystalline areas and the degree of crystallinity can be determined using X-ray diffraction (XRD) analysis.

$$X_c = \frac{I_{criss}}{I_{gen}} \times 100\% . \quad (2)$$

From the results, we can also calculate the lattice size formed.

$$D = \frac{K\lambda}{\beta \cos \theta} . \quad (3)$$

An XRD analysis of a film formed by drying a polymer solution at room temperature was conducted (Fig. 3).

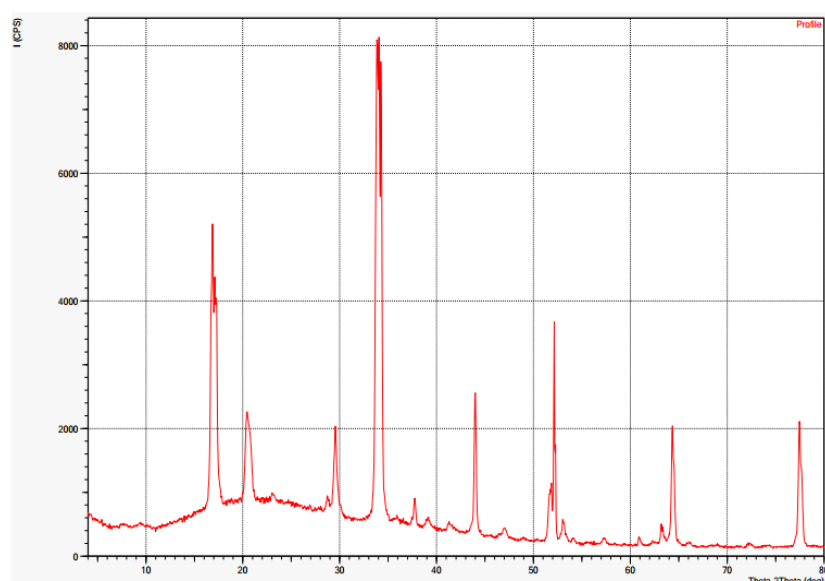


Figure 3. XRD image of polyacrylamide polymer film.

The XRD spectrum of this polyacrylamide provides crucial information about the crystalline structure of the material. Notably, the most intense peak around 30° represents the primary crystalline phase of polyacrylamide. This peak indicates that the distances between the atoms in the material's crystalline lattice are well-defined. Using these peaks, it was determined that the amount of crystalline phase in the polymer content is significant, and the sizes of the lattices were identified (Tab. 1).

Table 1. XRD spectrum analysis of polyacrylamide crystalline structure

Peak number	2Theta (degrees)	FWHM (degrees)	FWHM (radians)	Crystal size (Å)
1	17.0504	0.7365	0.012854	109.07
6	34.0265	0.7190	0.012549	115.55
14	77.4771	0.4371	0.007629	233.01

The location and intensity of each peak are critical as they provide complete information about the characteristics of the crystalline phases. The overall structure of the graph indicates that the XRD spectrum of polyacrylamide includes not only the crystalline phases but also the material’s amorphous characteristics. The amorphous phases are visible in the regions of lower intensity between the peaks, representing the non-uniform amorphous parts of the polymer structure.

Rheology. A solution of polyacrylamide in water was examined using an Anton Paar MCR 92 rheometer, across an angular frequency range from 0 to 700 rad/s. The dependence of shear stress and shear strain on frequency was studied (Table 2).

Table 2. Rheological properties of polyacrylamide solution

Point No	Angular Frequency [rad/s]	Storage Modulus [Pa]	Loss Modulus [Pa]	Loss Factor [1]	Shear Strain [%]	Shear Stress [Pa]	Torque [mN·m]
1	0.314	2.4435	48869	20000	0.00276	1.3476	0.005498
2	0.521	46799	11926	0.255	0.931	449.81	1.8352
3	0.866	19625	10192	0.519	0.208	45.897	0.18725
4	1.44	56971	36551	0.642	0.853	577.62	2.3566
5	2.38	43812	31773	0.725	0.886	479.77	1.9574
6	3.96	77604	58170	0.75	0.961	931.73	3.8013
7	6.57	1.02E+05	79830	0.783	0.977	1264.9	5.1607
8	10.9	1.19E+05	94252	0.794	0.986	1494.2	6.0962
9	18.1	1.37E+05	1.10E+05	0.801	0.997	1747.7	7.1304
10	30	1.52E+05	1.19E+05	0.787	1	1932.2	7.8831
11	49.9	1.62E+05	1.28E+05	0.791	0.976	2013.1	8.213
12	82.8	1.97E+05	1.51E+05	0.767	0.994	2465.4	10.059
13	137	2.25E+05	1.74E+05	0.773	0.995	2833.3	11.56
14	228	2.47E+05	1.96E+05	0.795	0.998	3145.6	12.833
15	379	2.51E+05	2.01E+05	0.801	1	3228.9	13.174
16	628	2.58E+05	2.14E+05	0.829	1	3360.4	13.71

The results graphically depict how the material’s stress and deformation change with varying angular velocities. It is evident from the graphs that the behavior of the material’s stress and deformation changes according to different laws at various angular frequencies (Fig. 4).

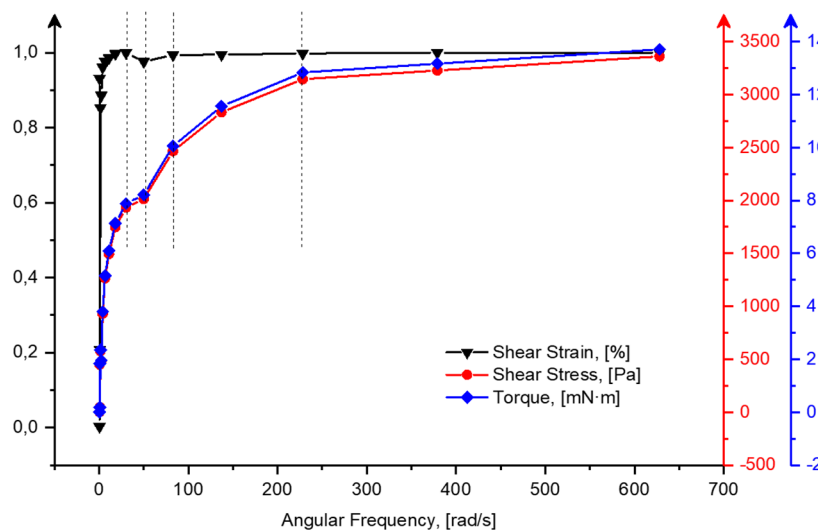


Figure 4. Dependence of rheological parameters on the angular frequency of rotation

At the beginning of the graph, the shear strain rapidly increases, reaching nearly 1.0 (100%) at approximately 100 rad/s, and then remains nearly constant. This indicates that the elastic phase of polyacrylamide quickly saturates and subsequently does not deform further.

The shear stress curve also shows an increase, rising with angular frequency and stabilizing around 3500 Pa. This suggests that polyacrylamide retains its elastic properties even at higher frequencies, and due to the considerable size of polyacrylamide molecules, elasticity becomes more pronounced with increasing frequency due to the ordering of their conformational state.

The dependence of the solution's internal friction coefficient on angular frequency was examined (Fig. 5). Initial viscosity values are very high (≈ 3000 mPa), decreasing almost exponentially with increasing frequency and stabilizing at around 500 mPa. This indicates that in the absence of external influences, the material's molecules form strong cohesion; as external forces increase, elasticity emerges and cohesion decreases. The material maintains its stability even under high strain, which is crucial for determining its application areas.

When we apply a shear stress to the liquid, we impart a pulse, which is transmitted through different layers of the liquid. Due to friction between the layers, the velocity of the liquid and its kinetic energy decrease. The transverse stress and shear velocity are proportionally linked through the coefficient of internal liquid friction. The kinetic energy in the system occurs due to internal cohesion or dynamic viscosity η [3].

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (4)$$

The viscosity of a liquid depends on pressure and temperature, generally increasing with rising pressure and decreasing temperature. We can observe how the internal friction coefficient changes according to different laws at various angular frequencies. The graph can be divided into areas where the internal friction coefficient changes according to three distinct laws. While the polyacrylamide polymer exhibits high viscosity at low angular frequencies, the viscosity decreases rapidly up to $12-15 \text{ s}^{-1}$ as the frequency increases, then decreases linearly between $178-180 \text{ s}^{-1}$, and remains nearly constant at higher frequencies.

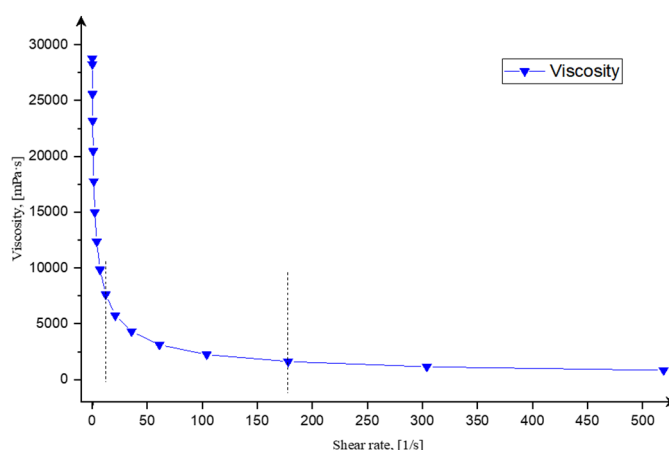


Figure 5. Relationship between sample viscosity and shear rate

The decrease in viscosity at high angular velocities is a characteristic of solutions containing long-chain molecular structures. At high velocities, the molecules' conformation aligns with the flow direction, and they begin to flow as parallel layers.

CONCLUSIONS

The rheological properties of the polyacrylamide polymer are analyzed with high precision using the state-of-the-art Anton Paar MCR 92 across an angular frequency range from 0 to 700 rad/s. The physicochemical properties of polyacrylamide, including its molecular weight, viscosity, and sensitivity to external influences, were studied.

The molecular structure and dimensions of the crystalline lattice of the polymer material were thoroughly investigated using IR spectroscopy and X-ray diffraction (XRD). The XRD spectra indicate that the high quantity of the primary crystalline phase of polyacrylamide aids in understanding the dissolution mechanism in the solvent. The results observed a rapid saturation of the material's elastic phase and a stabilization of shear stress around 3500 Pa, demonstrating polyacrylamide's ability to retain its elastic properties even at high frequencies. In conclusion, these analyses provide significant insights into the rheological properties and molecular structure of polyacrylamide.

Optimizations, including the introduction of various types of additives, are required for the application of polyacrylamide in the oil and gas industry, water purification systems, and pharmaceutical manufacturing. These findings also help in understanding the effective application of polyacrylamide produced by local manufacturers in different environments and contribute to advancing new achievements within the scientific community.

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РЕОЛОГІЧНІ ТА ФІЗИКО-ХІМІЧНІ ВЛАСТИВОСТІ ПОЛІАКРИЛАМІДУ: АНАЛІЗ ТА ЗАСТОСУВАННЯ

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У цьому дослідженні представлено поглиблену реологічну характеристику поліакриламідних полімерів, вироблених на місцевому рівні, використовуючи Anton Paar MCR 92 (модульний компактний реометр). Зразки полімерів систематично аналізували, щоб зрозуміти їх реакцію на різні зовнішні подразники. Використовуючи інфрачервону спектроскопію, склад полімеру був ретельно перевірений, забезпечуючи надійну оцінку його молекулярної структури та хімічної стабільності в різних умовах навколишнього середовища. Наші висновки з'ясовують значний потенціал поліакриламідів в різноманітних промислових застосуваннях, що пояснюється його адаптивними в'язкопружними властивостями та хімічною стійкістю. Наслідки цього дослідження є глибокими, що свідчить про збільшення користі поліакриламідів в областях, де потрібна точна модуляція поведінки матеріалу в динамічних умовах.

Ключові слова: поліакриламід; Anton Paar MCR 92 (модульний компактний реометр); реологія; гель; гідрогель; ІЧ-спектроскопія