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Ye.V. Blagikh¹, Zh.K. Sadakbayeva², A.N. Klivenko³,
Zh.A. Nurakhmetova¹, V.B. Sigitov¹, S.E. Kudaibergenov¹

¹*Institute of Polymer Materials and Technology, Almaty, Kazakhstan;*

²*Institute of Macromolecular Chemistry of the Academy of Sciences, Prague, Czech Republic;*

³*Shakarim State University of Semey, Kazakhstan*

(E-mail: skudai@mail.ru)

Development of composite hydrogel materials for cleaning the inner surface of pipelines

Flexible, mechanically strong composite hydrogel materials based on polyacrylamide hydrogel (PAAH), clay minerals (kaolin, bentonite and montmorillonite), poly-N-vinylpyrrolidone (PVP) and SiO₂ were developed for cleaning the inner surface of pipelines. The mechanical strength of composite hydrogels increases in the following order: PAAH-PVP > PAAH-Montmorillonite > PAAH-SiO₂ > PAAH-Bentonite. The results showed that the composite hydrogel samples are able to sustain more than 200 cycles of vertical deformation without damage. The hydrogel «pigs» selected according to the values of tensile strength and Young's modulus were tested on model «small» and «big» pipelines. The application of hydrogel «pigs» for cleaning the model pipelines proved to be successful. In contrast to mechanical analogues, hydrogel «pigs» pass freely through the pipelines of various shape and size, ensure necessary hydraulic pressure in the inner surface, provide explosion and fire safety, and absorb water along in the course of movement inside the pipeline. Their cleaning efficiency of the model pipelines from the asphaltene-resin-paraffin deposits (ARPD) was evaluated as 93–95 %. The scaled up hydrogel «pigs» were fabricated for cleaning of oilfield pipes. The proposed materials would be of interest for oil transportation companies due to cost-efficiency and technological feasibility.

Keywords: hydrogels, clay minerals, polyacrylamide hydrogel, composite materials, hydrogel «pigs», Young's modulus, model pipeline, cleaning effectiveness, asphaltene-resin-paraffin deposits.

Introduction

During the last decade, technical policies of oil transportation companies became more demanding regarding the longevity of the pipelines [1]. In the process of pipeline exploitation, the debris, sand and a mixture of asphaltene-resin-paraffin deposition (ARPD) are accumulated and deposited on the inner surface of the pipeline, leading to reduced capacity of the pipeline, low velocity of oil stream and increased pressure in the pipeline [1,2]. Additionally, water retention that occurs in the lower sections of the pipeline can cause corrosion process while accumulation of gas-air mixture in the upper sections of the pipeline can lead to explosion problems. The simultaneous transportation of crude oil and petroleum products in one and the same pipe is also a challenging task [3–5]. Periodic cleaning of pipelines by hydrogel «pigs» can significantly increase their productivity, prevent corrosion and extend their lifetime [6–8].

The pioneering works to strengthen the mechanical properties of hydrogels adding inorganic components were performed by Haraguchi [9, 10]. Composite gel is made from N-isopropylacrylamide; in its matrix, montmorillonite particles are immobilized. Mechanical characteristics of a gel with inorganic fillers are much better than that of a conventional gel. Mechanism of formation of the composite structures can be represented as a diffusion of acrylamide monomers to the layered clay structure [11–15]. After monomers are intercalated to the minerals, polymerization with simultaneous crosslinking of composite hydrogel materials

takes place. Nano- and microsized clay particles play the role of additional physical crosslinking centers. It leads to a significant increase in quality of mechanical properties of the composite materials.

Osada and co. [16–18] designed a series of double-network hydrogels with extremely high mechanical strength. This kind of nanocomposite hydrogel exhibited high transparency, high deswelling rate and extraordinary mechanical properties with up to $10^3\%$ of elongation ratio at break. Recently [19], physical hydrogels composed of polyampholytes demonstrating high toughness and viscoelasticity were developed.

In our earlier works [20–22], we have described the preparation and characteristics of composite materials based on PAAH and clay minerals. The present paper highlights the applicability of the composite hydrogel materials for purposes of cleaning the inner surface of pipeline from ARPD.

Experimental

Materials

Preparation of composite materials based on polyacrylamide hydrogel (PAAH), clay minerals, SiO_2 and PVP is reported elsewhere [20–22] (Fig. 1).

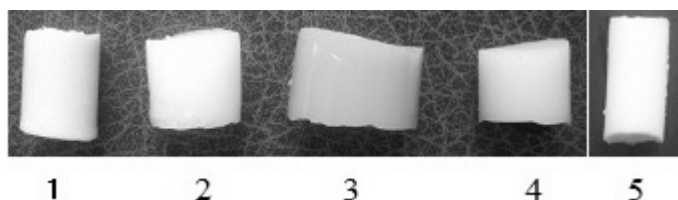
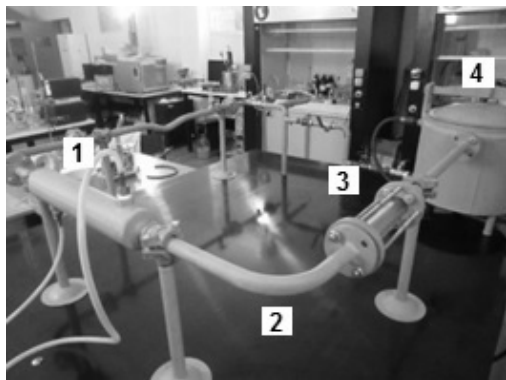


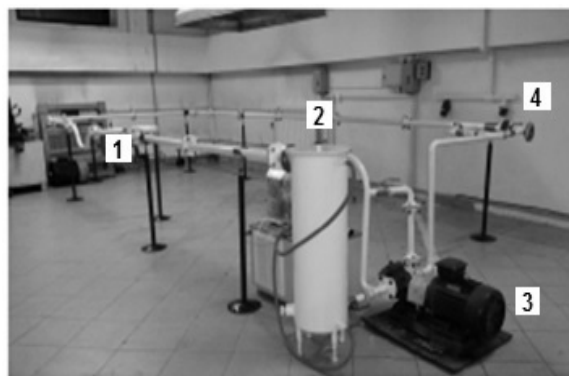
Figure 1. Samples of the composite materials based on PAAH and kaolin (1), SiO_2 (2), bentonite (3) montmorillonite (4) and PVP (5)

Two model pipelines with different length and diameter of the pipes, «Small» pipeline with $L = 3$ m, $d = 20$ mm) and «Big» pipeline with $L = 15$ m, $d = 40$ mm, were used for laboratory test of hydrogel «pigs» (Figs. 2 and 3).



1 — section for cooling of oil; 2 — steel pipe; 3 — section for visualization of oil flow; 4 — oil reservoir

Figure 2. «Small» model pipeline



1 — steel pipe; 2 — oil reservoir; 3 — pump; 4 — inlet for hydrogel «pigs»

Figure 3. «Big» model pipeline

Both «Small» and «Big» pipelines consist of oil reservoir, pump, steel pipe of different cross-section, equipped with valves and monometers, sections for cooling of oil and visualization of oil flow, inlet and outlet for hydrogel «pigs». In order to have the ARPD deposited, the crude oil was heated up to $60\text{ }^\circ\text{C}$ and circulated inside of a pipe for 2, 4 and 6 hours. The temperature of the cooling section was maintained at $5\text{ }^\circ\text{C}$. The heating and cooling regimes of oil in model pipe correspond to real conditions of oil transportation. As anticipated, some ARPD was deposited on the inner part of steel pipe leading to the reduction of the pipeline's capacity. After cleaning a pipe by hydrogel «pigs», the solid ARPD was weighed and its amount was calculated.

After circulation of crude oil inside of «Small» model pipeline during 2, 4 and 6 hours, the section was cooled at 5 °C, then dismantled and weighed. The amount of deposited ARP was calculated, and the efficiency of pipe cleaning (E) by hydrogel «pigs» was estimated using the formula (1):

$$E = \frac{m_2}{m_1} \times 100 \% , \quad (1)$$

where m_1 — is the mass of the pipe before ARP deposition (g); m_2 — is the mass of the pipe after ARP deposition at definite time (g).

Scaling-up of hydrogel «pigs» was performed in reinforced plastic oilfield pipe with internal diameter of 220 mm and length of 230 mm. The bottom of plastic oilfield pipe was plugged and filled with the mixture of acrylamide, crosslinker, initiator, appropriate clay minerals dispersed in distilled water. The polymerization reaction was initiated by addition of accelerator — N,N,N',N'-tetramethylethylenediamine and carried out at room temperature during 3–4 hours. The scaled-up composite hydrogel «pigs» are presented in Figure 4.



Figure 4. Scaled up composite hydrogel «pigs»

Results and Discussion

Testing on model pipeline

It should be noted that both «Small» and «Big» model pipelines were set up according to technical documentations of regular oilfield pipelines. As illustrated in Figure 5a, the gel «pig» successfully cleaned the inner surface of the pipe from corrosion deposits and mechanical impurities. Figure 5b shows the case when the «pigs» were used for cleaning the pipeline from ARPD.



Figure 5. Cleaning of pipe from mechanical impurities and corrosion deposits (a) and from ARPD (b)

The effectiveness of cleaning the model pipeline was compared with other composite hydrogel materials. As indicated in Table 1, the cleaning of the deposited ARP from Kumkol and Usen oil (Western Kazakhstan) with composite hydrogel «pigs» in dynamic regime showed 92–95 % effectiveness. The advantages of the proposed materials in comparison with mechanical scrapers are: the smooth passage through pipe sections with complex profile, the good hydraulic pressure inside of pipe, the sorption of water-salt mixtures accumulated inside of pipe, and explosion safety.

Cleaning effectiveness of hydrogel «pigs»

Composite hydrogels	ARPD deposition time, hour	ARPD deposited, g	ARPD removed, g	Effectiveness, %
PAAH/PVP-Bentonite	2	281±5	265±5	90±2
PAAm/PVP-SiO ₂	4	269±5	244±5	91±2
PAAm/PVP	6	255±5	238±5	92±2

From practical point of view, the most important parameter of hydrogel «pigs» is their mechanical properties. The selected samples exhibit a high stability and good tolerance towards mechanical stress. As illustrated in Figure 6, the mechanical strength of composite hydrogels increases in the following order: PAAH-PVP > PAAH-Montmorillonite > PAAH-SiO₂ > PAAH-Bentonite.

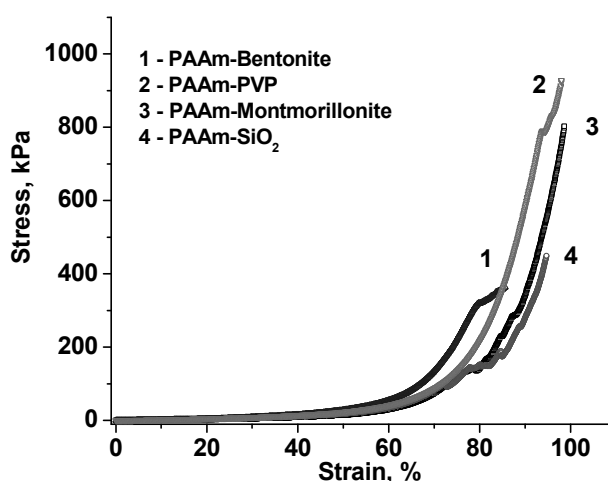


Figure 6. Compressive stress-strain curves of polyacrylamide hydrogels containing bentonite (1), PVP (2), montmorillonite (3) and SiO₂ (4)

The optimal hydrogel «pigs» selected for testing on model pipelines according to the values of tensile strength and Young's modulus are presented in Table 2.

Table 2

The Young's modulus and tensile strength of composite hydrogels used for model pipeline cleaning

Composite hydrogels	Mechanical properties	
	Young's modulus, kPa	Compressive strength, kPa
PAAH/PVP	5.89	791.3
PAAH/PVP-Bentonite	3.30	120.0
PAAH/PVP-SiO ₂	2.60	96.1

Usually inside of the real pipeline, the hydrogel «pigs» are subjected to high pressure during the movement. Therefore the stability of composite hydrogel materials under vertical stress was evaluated at constant cyclic deformation. The results showed that the samples are able to sustain more than 200 cycles of vertical deformation without damage (Fig. 7). It indicates that the materials have advanced mechanical properties and can be applied under oilfield conditions.

The cost of developed composite hydrogel «pigs» is compared with commercial available gel samples in Table 3. The diameter of gel «pigs» corresponds to diameter of the pipe used for oil transportation. Evidently, the composite hydrogel «pigs» developed at the Institute of Polymer Materials and Technology are more cost-effective than that of «SamTechnoOil» (Russia) and «Aubin» (UK) companies. At present the manufacturing instructions for production of hydrogel «pigs» were developed. In 2015, the Committee of industrial development and safety of the Ministry of investment and development of the Republic of Kazakhstan issued a permission for the production and application of hydrogel «pigs» («PIG-1») for cleaning of real pipelines.

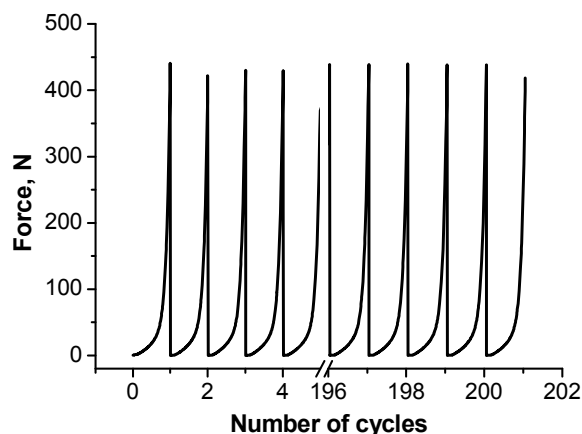


Figure 7. The effect of the number of compression cycles on the elastic deformation of PAAH-PVP composite hydrogel

Table 3

Characteristics and costs of hydrogel «pigs» developed by various companies

Company	Diameter of gel «pigs», mm	Volume of gel «pigs», mm ³	Price, USD
«SamTechnoOil» (Russia)	1200	100	295
«Aubin» (UK)	700	1000	4912
«PIG-1» (IPMT «Kazakhstan»)	377	750	455

Conclusions

Flexible, mechanically stable composite hydrogel materials based on crosslinked polyacrylamide, clay minerals and PVP were developed. The mechanical strength of composite hydrogels increases in the following order: PAAH-PVP > PAAH-Montmorillonite > PAAH-SiO₂ > PAAH-Bentonite and demonstrates that PAAH-PVP semi-interpenetrating networks withstand the highest compressive load. Particularly, the PAAH-PVP can sustain more than 200 cycles of vertical deformation without damage. Composite hydrogel «pigs» were tested for their cleaning properties on «Small» and «Big» model pipelines; the efficiency of ARPD, corrosion deposition and mechanical admixtures removal from the inner surface of the pipe was in the range of 93–95 %. Additionally, permission for production and application of hydrogel «pigs» («PIG-1») for cleaning of real pipelines was issued.

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Е.В. Благих, Ж.К. Садакбаева, А.Н. Кливенко,
Ж.А. Нұрахметова, В.Б. Сигитов, С.Е. Құдайбергенов

Құбырөткізгіштердің ішкі беттерін тазартуға арналған композициялық гидрогель материалдардарын жасап шығару

Полиакриламид (ПААГ), поли-N-винилпирролидон (ПВП) және сазды минералдар (каолин, бентонит және монтмориллонит) негізінде композициялық гидрогель материалдарын жасап шығару, олардың механикалық қасиеттерін зерттеу және мұнай құбырларының ішкі қабатын тазарту үшін механикалық берік, иілгіш және майысқақ қырғыштар ретінде қолдану нәтижелері берілген. Композиттік гидрогельдердің механикалық қасиеттері келесідей артатыны анықталды: ПААГ-ПВП > ПААГ-монтмориллонит > ПААГ-SiO₂ > ПААГ-бентонит. Нәтижелер көрсеткендей, композиттік гидрогельдердің үлгілері жоғарғы механикалық төзімділікке ие, олар айтарлықтай, бүлінусіз 200 тік деформациядан артыққа төзе алады. «Үлкен» және «кіші» құбырларды тазартуға арналған гидрогельдік материалдарды таңдау мен тестілеу сығылу мен созылудағы төзімділік шектеулігі мен Юнг модулінің онтайлы мәндеріне сәйкес жасалған. Композициялық гидрогель материалдары тазарту құрылғылары ретінде модельді мұнай құбырында ұтымды қолданылды. Механикалық аналогтарына қарағанда, гидрогельді тазартқыштар әр түрлі пішіндегі және өлшемдегі құбырлар арқылы оңай өтеді, ішкі бетке қажетті гидравликалық қысымды қамтамасыз етеді, жарылу қауіпсіздігін қамтамасыз етеді және құбырлардың ішкі бетіндегі суды өзіне сіңіреді. Модельді құбырөткізгіштерді асфальтенді шайырлы парафинді қалдықтардан (ARPD) және механикалық қоспалардан коррозиялық қалдықтардан тазартуда олардың тиімділігі 93–95 % құрады. Өндірістік мұнай құбырларын тазартуға арналған гидрогельдік материалдарды масштабтау жүргізілді. Ұсынылып отырған материалдар экономикалық тиімділігі және технологиялық жүзеге асырылуына байланысты мұнай тасымалдаумен айналысатын компаниялардың қызығушылығын тудырады.

Кілт сөздер: сазды минералдар, полиакриламид гидрогелдері, композициялык материалдар, гидрогелді «қырғыш», Юнг модулі, модельді құбырөткізгіш, тазарту дәрежесі, асфальтен-шайыр-парафин шөгінділері.

Е.В. Благих, Ж.К. Садакбаева, А.Н. Кливенко,
Ж.А. Нурахметова, В.Б. Сигитов, С.Е. Кудайбергенов

Разработка композиционных гидрогельных материалов для очистки внутренней поверхности трубопроводов

Разработаны гибкие, эластичные и механически прочные композиционные гидрогелевые материалы на основе полиакриламидного гидрогеля (ПААГ), глинистых минералов (каолин, бентонит и монтмориллонит), поли-N-винилпирролидона (ПВП) и SiO₂ для очистки внутренней поверхности трубопроводов. Механические свойства композитных гидрогелей увеличиваются в следующем порядке: ПААГ-ПВП > ПААГ-монтмориллонит > ПААГ-SiO₂ > ПААГ-бентонит. Результаты показали, что образцы композитных гидрогелей обладают высокой механической прочностью и без существенных разрушений могут выдержать более 200 вертикальных деформаций. Тестирование и отбор гидрогелевых «скребков» для очистки «малого» и «большого» трубопроводов осуществлялись в соответствии с оптимальными значениями предела прочности при сжатии или растяжении и модуля Юнга. В лабораторных условиях использование композитных материалов в качестве гидрогелевых «скребков» для очистки модельного трубопровода оказалось успешным. В отличие от механических аналогов, гидрогелевые «скребки» свободно проходят через трубопроводы различной формы и размера, обеспечивают необходимое гидравлическое давление на внутреннюю поверхность, обеспечивают взрывобезопасность и поглощают воду при движении по трубопроводу. Эффективность гидрогелевых «скребков» при очистке модельного трубопровода от механических примесей, коррозионных отложений и асфальтен-смоло-парафиновых отложений (АСПО) составила 93–95 %. Проведено масштабирование гидрогелевых «скребков» для очистки промышленных нефтепроводов. Предлагаемые материалы будут представлять интерес для нефтяных компаний, занимающихся транспортировкой нефти, благодаря экономической эффективности и технологической осуществимости.

Ключевые слова: глинистые минералы, полиакриламидные гидрогели, композиционные материалы, гидрогелевый «скребок», модуль Юнга, модельный трубопровод, эффективность очистки, асфальтен-смоло-парафиновые отложения.

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