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Combination of fluorescent and spin labels: a powerful method for the optimization of hydrophilic membranes for the separation of oil-in-water emulsions

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Abstract

A new method for assessing the quality of fibre coating based on a combination of fluorescence microscopy and electron paramagnetic resonance is presented in this work. An influence of the carboxymethylcellulose/polyvinylamine gel preparation method on the mobility of the spin label was established. The mobility of the spin label changes from 3.5 ns in the case of a polyvinylamine solution to 12.8 ns in the case of a cross-linked gel on the surface of the glass fibre. A qualitative relationship was found between the mobility of the spin label in the gel applied to the glass fibre and the rate of spreading of crude oil over its surface. This method can be used to make membranes for the separation of water-in-oil emulsions.

Keywords

fluorescent label
spin label
oil-in-water emulsion
carboxymethylcellulose
polyvinylamine

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Key findings

- The mobility of the spin label depends on the method of obtaining the CMC/PVAm gel on the surface of the glass fibre.
- There is a correlation between the mobility of the spin label in the CMC/PVAm and crude oil spreading.
- The fluorescent mark in the CMC/PVAm gel shows defects when it is distributed on the surface of the glass fibre.

1. Introduction

Membrane technologies have found widespread use for the separation of water-oil emulsions. The use of membranes has a number of advantages over other water purification technologies, as they allow for high technological efficiency, multiple-use capability and environmental friendliness [1, 2]. For example, they are used to collect crude oil and petroleum products from the surface of water during emergency response, filter contaminated water, and separate process water, such as cutting fluids [3–5]. In the manufacture of membranes, various materials can be used, including ceramics and metal mesh [6, 7], but they do not meet modern requirements for environmental safety and biodegradability of materials.

Therefore, in recent decades, membranes based on biopolymers have been the focus of research groups involved in water purification [1]. Such membranes can be made entirely of biopolymer in the form of aerogel or thin filaments [8, 9]. However, this approach requires a lot of material and is expensive. A more practical method involves coating fabrics or nonwovens with a hydrophilic polymer [10]. A good example of this approach is the coating of textile fibre with agarose [11], glucomannan [12], a combination of ovalbumin and tannic acid [13], or polydopamine and chitosan [14]. In all cases, a hydrophilic coating is formed on the surface of the fibre, which prevents oil droplets from spreading over the surface. As a result, water passes freely through such a membrane, and the oil forms spherical droplets that are repelled from the surface of the membrane and separated from the water. The separation quality reaches 99% and the membrane can be reused up to 40 times [13].

The quality of separation of oil-water emulsions very much depends on the quality of the coating of the fibres with a hydrophilic polymer and on the presence of various defects on the surface. Oil droplets spread over the surface of such defects, making the material more hydrophobic and reducing its effectiveness in separating emulsions [15]. The characteristics of the gel on the surface of the fibres and its density and adhesion strength to the fibre, are also of great importance [16]. Therefore, methods that make it possible to determine the qualitative characteristics of the coating on the fibre are crucial in the manufacturing of hydrophilic membranes.

A convenient method for visualizing gel coatings with a thickness of less than 1 μm on the fibre surface is the introduction of fluorescent labels [17, 18]. This method not only allows finding defects on the surface, but also determines the qualitative characteristics of the gel, such as its density and the mobility of the molecules in it. Fluorescence methods provide information on the dynamics of molecules on the surface, but, like all optical methods, have certain limitations for a sample. In particular, the surface should not contain pores, be flat and, in most cases, transparent [19]. As opposed to optical methods, which have some limitations for studying porous materials, electron paramagnetic resonance spectroscopy (EPR) allows observing paramagnetic molecules inside a non-paramagnetic matrix of any morphology. Previously, the spin label technique was widely used in the investigation of the dynamic properties of proteins [20, 21] and polysaccharides-coated nanoparticles [22, 23].

In this paper, we propose a method to evaluate the quality of hydrophilic polymer coatings based on carboxymethyl cellulose and polyvinylamine (CMC/PVAm) on fibres using the spin and fluorescent labelling method. To obtain ultrathin films on the surface, an approach based on layer-by-layer deposition of polymers with opposite charges on the surface of the glass fibre was used. The purpose of the study was to identify the correlation between the mobility of EPR tags and the ability of the material to retain crude oil on the surface of the fibre. Overall, we propose a new analytical method to evaluate the quality of polymer gel-coated membranes.

2. Materials and methods

The stable radical 4-iodoacetamide-2,2,6,6-tetramethylpiperidine-N^1-oxyl was synthesized in the laboratory of nitrogenous materials of the Institute of Organic Chemistry (Novosibirsk) by the procedure described in [24]. Carboxymethyl cellulose (low viscosity polyanionic cellulose with degree of substitution 0.98, purity 95%, pH of 1% solution in water of 7.2 and apparent viscosity 19.4 mPa·s) was purchased from Henan Ocean Chemical Technology, China. Polyvinylamine (PVAm) of purity 98% was purchased from BASF, Germany as a 30% solution of salt with formic acid in water. Other materials include a dialysis membrane for molecular weights of 8 kDa and 12 kDa (Orange Scientific, Belgium) and various organic reagents of analytical grade (Acros Organics, Belgium): formaldehyde, 95% ethanol, calcium chloride, hydrochloric acid, sodium hydroxide, phosphate buffer, acetic acid, deionized water.

2.1. Preparation of PVAm labeled with rhodamine

PVAm labeled with rhodamine B was obtained by preparing mixture of 850 μl of polyvinyl amine (30% solution in water), 1 ml of acetonitrile and 50 μl of pyridine in a small vial. After that, 1 mg of rhodamine B was added to the mixture and dissolved. The mixture was left overnight for the reaction to proceed.

2.2. Preparation of PVAm with spin label

PVAm labeled with spin dye was obtained by preparing a mixture of PVAm solution 850 μl, acetonitrile 1ml, distilled water 2 ml and pyridine 50 μl. After that, 10 mg of 4-iodoacetamide-2,2,6,6-tetramethylpiperidine-N^1-oxyl was dissolved in the mixture. The mixture was left overnight in a dark place allowing the reaction to proceed successfully. A polymer solution with the cross-linked label was used to prepare a gel with CMC.

2.3. Preparation of CMC/PVAm film

CMC/PVAm titrated sample was prepared by titrating 15 ml of 0.5% CMC with 3 ml of 4.4% PVAm until the massive precipitation. After that, the precipitate was collected and dried in the oven at 55 °C. The dried CMC/PVAm films were utilized for further studies.

2.4. Coating of glass fibres with CMC/PVAm

Layer-by-layer deposition was used for fibre coating with CMC/PVAm. Fiberglass of size 2 cm x 2 cm was dipped consequently in different solutions. Three different samples were prepared.

Preparation of sample **S1**. The glass fibre was placed in a 0.5% PVAm solution for 10 min. Then the excess solution was removed using filter paper, and the sample was washed with distilled water. After this, the sample was dipped into a 0.5% CMC solution for 20 min, and the excess was removed using filter paper and washed with water. This coating cycle was repeated three times.

Preparation of sample **S2**. The glass fibre was placed in a 0.5% PVAm solution for 10 min. Then the excess solution was removed using filter paper and the sample was washed with distilled water. After this, the sample was dipped into a 0.5% CMC solution for 20 min, and the excess was removed using filter paper and washed with water. Then 0.1% formaldehyde solution of pH 3 was utilized for the last dipping. This coating cycle was repeated three times.

Preparation of samples **S3** and **S4**. These samples were prepared similarly to the sample **S2** using 0.5% and 1% formaldehyde solution.

Preparation of sample **S5**. The glass fibre was placed in a 0.5% PVAm solution for 10 min. Then the excess solution was removed using filter paper and the sample was washed with distilled water. After this, the sample was dipped into a 0.5% CMC solution for 20 min, and the excess was removed using filter paper and washed with water. The sample was dried in the oven at 50 °C for 40 min, then 0.1%

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formaldehyde solution of pH 3 was utilized for the last dipping. This coating cycle was repeated three times. Preparation of sample **S6**. These samples were prepared similarly to the sample **S5** using 1% formaldehyde solution.

2.5. Fluorescent microscopy

Filaments of glass fibre were utilized for better observation of the gel on the surface. Layer by layer method was used. First, the glass fibre filaments were dipped in 0.3% PVAm labeled with rhodamine B, then it was dipped in 0.5% solution of CMC. The glass fibre filaments were immediately observed under the microscope Altami LUM 1 LED. The prepared slide was imaged under a 40X fluorescent lens.

2.6. EPR spectroscopy

EPR spectra were recorded with an Adani PX-100 spectrometer at room temperature. Computer simulation of the room temperature spectra was performed taking into account both rotational mobility of the chain of polymer layer on fiberglass and mobility of the paramagnetic fragment about the anchor group. The ODFR4 software developed by Prof. A. Kh. Vorobiev (Chemistry Department, Moscow State University) was used [25]. The magnetic parameters of spine label used for computer simulation were obtained from [26]. The concentration of spin-labeled polymer (PVAm) in the solution did not exceed $5 \cdot 10^{-4}$ M in order to avoid dipole–dipole broadening of the spectra.

2.7. Nuclear magnetic resonance (NMR)

^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) spectrometer in D_2O at 70 °C. To record the spectrum, 8 mg of both pure polymers, CMC and PVAm, were dissolved in 500 µl D_2O separately and mixed immediately before the start of the experiment.

2.8. Fourier-transform infrared spectroscopy

The spectra of CMC, PVAm and CMC/PVAm, were obtained by placing a sample of the film made of each compound in FTIR setup (Bruker Alpha FT-IR Spectrometer) equipped with an attenuated total reflectance (ATR) accessory and zinc selenite crystals. The samples were transferred directly into the ATR compartment, and the result was obtained by combining 24 scans. The spectra were recorded between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}.

2.9. Oil spreading test

Crude oil was used for oil spreading test. The test was done for the three types of samples: dried polymer films, samples (**S1**, **S4**, **S6**) aged in water at pH = 3 and same samples aged at pH = 8. The samples aged at pH = 7 were dipped into the distilled water with pH = 3 or pH = 8 before the test. The drop of oil (20 µl) was placed in the center of each sample using the micropipette. Then the spreading time and the nature of spreading were detected.

3. Results and Discussion

The experimental methodology we developed included three stages. At the first stage, polymer samples containing EPR spin labels and fluorescent labels were obtained. The nonwoven base was then coated with a polymer gel, and two samples were prepared. One of them contained an EPR spin label, the other – a fluorescent label. At the third stage, three samples were taken from different parts of the material, mixed, and analysed using an EPR spectrometer and a fluorescence microscope. At the last stage, the rate of spreading of a drop of crude oil over the surface of the material was assessed, and this data was correlated with the measurement results. This approach made it possible to identify the relationship between the mobility of the label and the fluorescence intensity, on the one hand, and the retention ability of the material in relation to crude oil, on the other.

Glass fibre was chosen as a model substrate for applying the polymer because this material provides good gel adhesion due to the hydrogen bonds of hydroxyl groups on the surface and, at the same time, is an inert base for determining EPR and fluorescence labels. Another feature of this material is that, when soaked in water, it retains crude oil very poorly. Therefore, any coating defects and changes in the properties of the gel are clearly visible when conducting experiments with this substrate. When moving from model materials to real materials for making membranes, coatings will be applied to dense cotton fabric, such as belting.

To apply the gel to glass fibre, a method of layer-by-layer deposition of polymers with opposite charges was used. For this purpose, carboxymethyl cellulose (CMC) and polyvinylamine (PVAm) were chosen. To evaluate the suitability of this material for coating glass fibres and obtaining IR and NMR spectra, thick films were first produced by casting. When using aqueous solutions of these polymers and subsequent casting, an insoluble film is formed on the surface of the fluoroplastic after drying. Crude oil is well retained on the surface of a wet film, which makes these materials promising for the production of the target membranes. Figure 1 shows that the oil drop retains a spherical shape and does not spread over the surface of the PVAm film. In its turn, CMC film also retains a drop of oil, but has high mechanical strength, too. When casting a PVAm film onto a glass surface, the formation of a durable coating with good adhesion was observed. Thus, the possibility of using this composition for application to glass fibre was determined.

Previously obtained films of the original polymers (PVAm and CMC) and their mixture were used to record IR spectra. The bands obtained for the CMC/PVAm film were compared with those of the starting polymers (Figure 2). In the spectrum for CMC, characteristic peaks were observed at 1045, 1320, 1416, 1594, and 2926 cm^{-1}.

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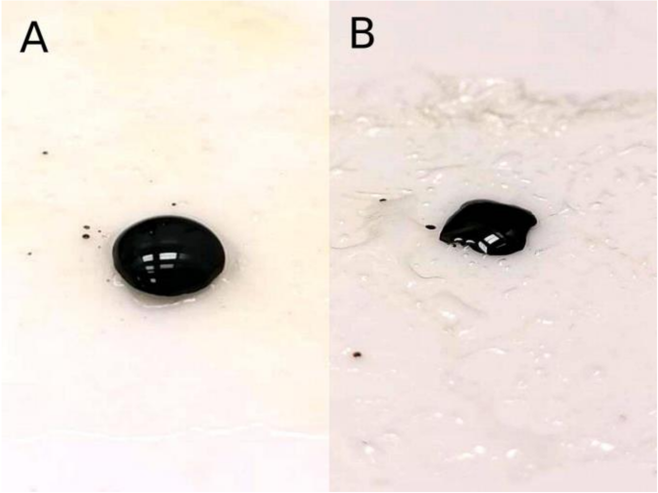

Figure 1 Oil droplet on the surface of PVAm film (a) and CMC film (b).

The intense peak at 1045 cm^{-1} corresponds to the stretching vibrations of the ether (C–O–C) group present in CMC. Also, the two short peaks at 1320 cm^{-1} and 1416 cm^{-1} are due to the symmetric stretching of alkyl groups, whereas the middle peak at 1594 cm^{-1} corresponds to the carbonyl group (C=O) present in CMC. Additionally, the peak at 2926 cm^{-1} arose due to the asymmetric stretching of C–H groups.

The PVAm spectrum (Figure 2) is characterized by the adsorbed peaks at 1375, 1610 and 2922 cm^{-1}. The band at 1610 cm^{-1} corresponds to the formamide group (CO–NH) present in this polymer as a result of incomplete hydrolysis. The peak at 1375 cm^{-1} corresponds to the bending vibration of the amine group (NH_2) and the one at 2922 cm^{-1} – to the asymmetric C–H stretching, respectively. The CMC/PVAm film also contains these bands, indicating the formation of the blend.

To record the NMR spectra, solutions of both polymers in deuterated water were mixed immediately before recording the spectrum. In this case, it was possible to obtain the spectrum of a sample that was insoluble under normal conditions (Figure 3). ^{1}H NMR spectroscopy revealed the set doublets in the spectra between the regions 4.2 ppm and 4.4 ppm can be assigned to the anomeric (α) carbon of the carboxymethyl cellulose. Also, the signals between 3.5 ppm and 4.2 ppm of the spectra represents the carboxymethyl (–OCH_2COO–) groups and the glucose backbone of CMC. Elsewhere, the characteristic peak found at 1.61 ppm corresponds to the protons of the methylene group of PVAm. Additionally, the peak at 8.34 ppm on the spectra corresponds to the protons of the formamide group of PVAm.

To obtain the polymer with a fluorescence label, rhodamine B isothiocyanate was used, which is a derivative with a side substituent active towards the amino group. A solution of the label in an organic solvent was added to an aqueous solution of polyvinylamine in water in the presence of a pyridine catalyst. The progress of the reaction was monitored chromatographically by the disappearance of the label in the solution, and the labelled polymer was purified using dialysis.

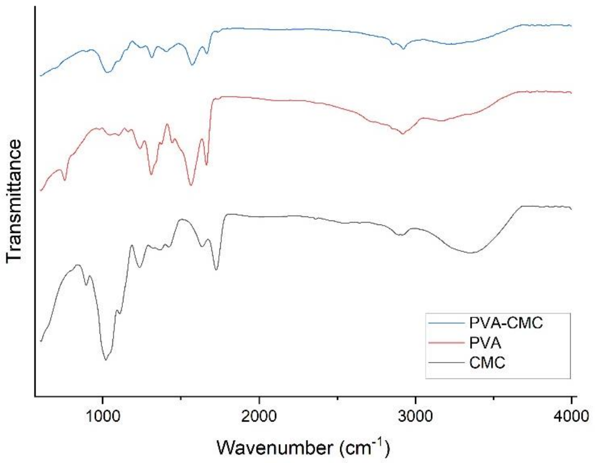

Figure 2 FTIR spectra of the samples: CMC/PVAm film, polyvinyl amine, carboxymethyl cellulose.

To obtain gel coatings with a fluorescent label, we used a sequential application of PVAm and CMC to the surface of the glass fibre from solutions of various concentrations. After each dipping into the solutions, the fibreglass sample was washed with distilled water. Figure 4 shows the photographs of the sample **S1** obtained using a fluorescence microscope for various polymer concentrations and coating cycles. As can be seen in photograph 4.3, when the concentration of the PVA solution is increased to 5%, the formation of beads is observed at the point of contact of the fibres. At the same time, reducing the concentration of working solutions below 0.5% led to incomplete coverage of the fibres. As can be seen in photographs 4.1 and 4.2, the thickness of the coating can be changed by adjusting the number of coating cycles. After a series of experiments, it was found that three cycles provide the optimal coating quality without defects. In this case, it is necessary to follow the order of application of the polymers, where the positively charged PVAm should be the first. Otherwise, peeling of the coating is observed as seen in photograph 4.4. Thus, the method allows you to visualize the gel coating on the surface of the fibre and determine the optimal concentration of solutions for its application.

The method of applying the gel to the fibres largely determines the properties of membranes for separating oil-water emulsions.

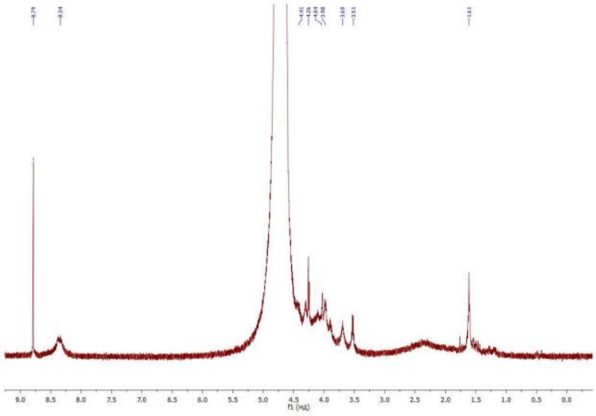

Figure 3 ^{1}H NMR spectrum of CMC/PVAm blend in D_2O.

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Therefore, several types of samples were prepared in this study. In the case of sample **S1**, the coating was applied to the fibres similarly to the method described above by sequential processing in PVA and CMC solutions, followed by washing with distilled water. In this case, we used the optimal concentrations of polymers that we found, and the PVA contained a spin label.

In the case of samples **S2**, **S3** and **S4** the resulting samples were additionally treated with an aqueous solution of formaldehyde with a concentration of 0.1, 0.5 and 1%, respectively. Samples **S5** and **S6** were first dried at a temperature of 50 °C and then treated with an acidified solution of formaldehyde. Formaldehyde was used to form cross-links between polyamine and cellulose polymer chains. At the same time, pre-drying made it possible to obtain a denser gel. Using this approach allowed obtaining samples with different properties. Next, the mobility of the spin label was studied using EPR methods.

A stable radical 4-iodoacetamide-2,2,6,6-tetramethyl piperidine-N^1-oxyl was used to determine the mobility of the polymer chains containing a spin label in gel samples on the fibre surface. The spin label was added to the PVAm sample before applying it to the surface of the glass fibre, so the label was covalently adhered to the polymer. The EPR spectrum of a spin label in a buffer solution and after adsorption on the polysaccharide, as well as the results of spectra simulation, are shown in Figure 5. The shape of the lines of the EPR spectra indicates a change in the rotational mobility of the nitroxide fragment after its attachment to the polymer, which indicates the successful completion of the reaction of the covalent addition of the nitroxide radical to functional groups of the polymer. The characteristics of the rotational mobility of the radicals are presented in Table 1. The signal of the spin label attached to the polymer was described taking into account both the internal rotational mobility of the polymer chains and the mobility of the paramagnetic nitroxide moiety around the anchor group. The mobility of the label around the anchor group was described as quasi-librations – high-frequency, low-amplitude oscillations of the paramagnetic group around the main magnetic axes of the nitroxide fragment. The quasi-libration model is used to calculate the EPR spectra of spin labels introduced into proteins [27, 28]. When evaluating the mobility of the spin label around the anchor group, the same values of libration mobility were used for all samples of the spin-labelled polymer membranes, which means that the difference in the shape of the lines in the EPR spectra is due to a change in mobility directly in the polymer chains. Applying cellulose polymer to glass fibre slightly reduces the mobility of the polymer chains (Table 1). After the cross-linking reaction, the EPR spectra (Figure 5) show broadening and bifurcation of the low-field component, which indicates a decrease in the mobility of the polymer chains and preservation of the mobility of the nitroxide fragment around the anchor group. The parameters for computer simulation of these spectra are presented in Table 1.

The selected samples **S1**, **S4** and **S6** coated with CMC/PVAm gel were tested for the rate of oil spreading on their glass surface. This method allows us to determine the wettability of the surface of a nonwoven material with an organic solvent. Three types of oil were used for the test: light oil, heavy oil and sour oil. Wet glass fibre is well wetted by oil; a drop applied to the material is instantly distributed over its surface. Sample **S1** holds oil better; the drop does not immediately spread over the surface and is easily washed off with running water after complete distribution over the surface (Figure 6).

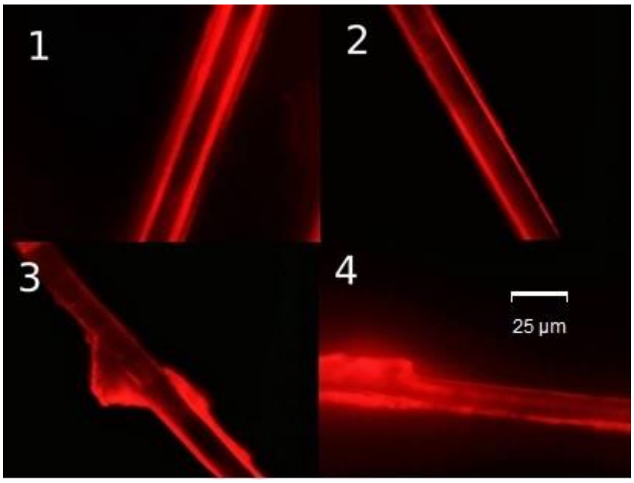

Figure 4 Optimization of sample **S1** synthesis based on CMC/PVAm gel containing rhodamine B.

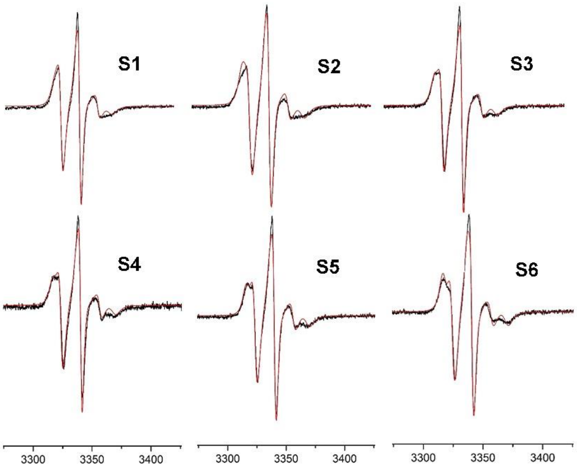

Figure 5 EPR spectra of CMC/PVAm gels (experimental spectra in black, calculated in red).

Table 1 Dynamic parameters of the EPR spectra of a nitroxide radical covalently bound to PVAm.

Sample	Rotational correlation time, ns	Libration
Radical in solution	0.05	0
Radical in PVAm gel	3.5	50.3
S1	8.3	50.3
S2	8.8	50.3
S3	9.3	50.3
S4	9.8	50.3
S5	11.1	50.3
S6	12.8	50.3

The retention ability is even more pronounced for samples **S4** and **S6**; in this case, the drop does not spread over the surface of the material for several minutes (Table 2). This correlation is well expressed for light and heavy oils and is less noticeable for high-sulphur oils. Apparently, sulphur compounds dissolve in the gel, making it more hydrophobic.

It should be noted that the material retains oil well only in a certain pH range, from 2 to 6. Under alkaline conditions at pH greater than 8, all samples showed low retention capacity in relation to all types of oil used in the experiment. This is due to a change in surface charge, which affects the attraction of oil droplets to the surface. The oil also spreads well over the surface of the sample, which had local coating defects identified using a fluorescent label.

The combined use of the two methods makes it possible to draw conclusions about the quality of application of the gel to the surface of materials and to select the most optimal methods of coating. In addition, this method allows us to take samples from various points on the fibre surface, revealing uniformity in the gel coating and the absence of defects. The sample volume required for analysis does not affect the properties of the fibre materials and allows testing for retention capacity. Using this method, two parameters can be determined: the uniformity of the gel distribution on the surface of the fibre and the presence of local defects. It is capable of identifying small surface defects that affect interaction with oil droplets. Our studies have shown that there is a qualitative relationship between the mobility of the spin label and the retention capacity of the material towards crude oil. The less mobility the EPR label exhibits in the gel, the longer it takes for the oil to spread over the surface of the fibres. The method can be successfully applied to various types of oil. The next step in our research will be the study of real fabrics used as substrates for the production of membranes for the separation of oil-in-water emulsions.

4. Limitations

In this study, glass fibre was used as the substrate due to its smooth surface and regular shape. This made all stages of the gel application and identification process easier. However, glass fibre can only be used to a limited extent in industrial filters for separating water-in-oil emulsions due to the insufficient mechanical strength of the fibres. Previously, we chose cellulose as the main material for the manufacture of such membranes due to its combination of mechanical strength and the possibility of recycling in nature [29, 30]. Therefore, the next step in the development of this method will be the use of cellulose fibres that have an irregular shape.

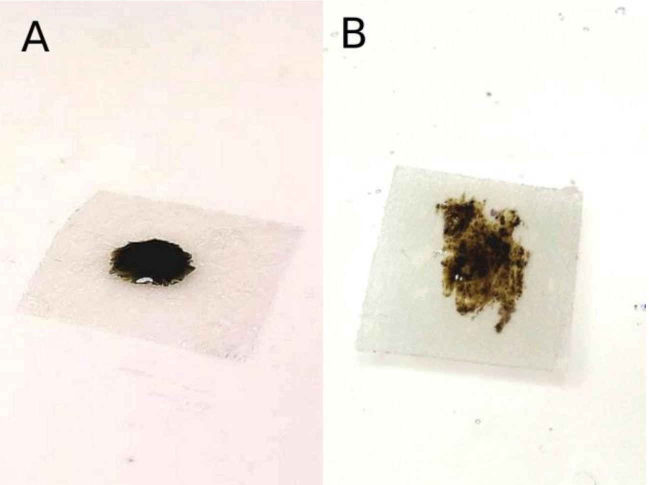

Figure 6 Oil spreading test: sample **S6**, Arabian light oil, 120 s (a); sample **S1**, Arabian light oil, 30 s (b).

Table 2 Retention time of various crude oils on the fiberglass surface coated of CMC/PVAm gel samples.

Sample	Retention time, s			
	Heavy oil	Light oil	Sour oil	Heavy oil, pH 8
Glassfiber	5	6	10	8
S1	30	25	35	20
S4	240	205	90	25
S6	410	360	120	25

5. Conclusions

In this study, it was possible to establish a qualitative relationship between mobility of the spin label in the CMC/PVAm gel applied to the glass fibre and the rate of spreading of crude oil over its surface. Thus, the mobility of the spin label can provide information on the possibility of using a fibre materials coated with a hydrophilic CMC/PVAm gel for the effective separation of water-in-oil emulsions. The additional introduction of a fluorescent label into the polymer structure makes it possible to identify coating defects, such as peeling of polymer films and uneven distribution of the gel over the fibre surface. In general, the combination of two labels, fluorescent and spin, makes it possible to efficiently assess the quality of fibre coating with a polymer gel based on CMC/PVAm.

• Supplementary materials

No supplementary materials are available.

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• Conflict of interest

The authors declare no conflict of interest.

• Additional information

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