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**MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS**

Study of Properties of Film Materials Based on Cellulose and Polyurethane Rubbers for Drainage of Oils

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Abstract—The use of both cellulose and polyurethane rubbers of the PU-8TB and PU-8A grades is discussed in the work to create film materials for draining oils. By the method of IR spectroscopy, the chemical interaction between the hydroxyl groups of cellulose and the carboxyl groups of polyurethane rubber is confirmed. Peculiarities of the thermal properties of the films are studied, which make it possible to speak of the repeated regeneration of materials from absorbed moisture without their destruction. The synthesized film materials have increased elasticity, hydrophilicity, and oleophobicity in comparison with the original cellulose film, which allows them to be used as sorbents and membranes in the field of oil and gas production. The research results showed that polyurethane rubbers PU-8TB and PU-8A, when combined with cellulose, act as functional additives in the manufacture of films capable of removing water from oils.

Keywords: polymer films, cellulose, polyurethane rubbers, hydrophilicity, oleophobicity, drainage of oil/water emulsions

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One of the most common methods for increasing the efficiency of oil production is the injection of water into the reservoir with the aim of increasing reservoir pressure and the subsequent displacement of oil to the bottom [1–3]. Despite its advantages, this method leads to water entering the pumped oil, which entails an increase in operating costs aimed at their separation, as well as due to corrosion of metal equipment. Nevertheless, water is contained in the reservoir oil, even if the process of water injection is completely excluded during production [4]. The use of polymeric materials with hydrophilic properties for draining oils may be one of the most promising solutions to this problem.

Oil drainage and separation of their emulsions in water can be carried out in two ways [5–7]. In the first case, polymer products with a hydrophobic and at the same time oleophilic surface are used, which are wetted and pass oil, but repel water. Moreover, the absorption of a part of the oil by the material leads to its pollution and the impossibility of complete regeneration. The use of hydrophilic and at the same time oleophobic polymeric materials that repel oil but pass or absorb water allows this problem to be avoided due to the formation of a hydrating layer near the surface of the material

Currently, the most effective way to quickly separate water and oil is to use various sorbents on an organic or inorganic basis. The use of such materials is limited by their high cost, finely dispersed form, and the difficulty of utilizing absorbers [8–10].

Cellulose (C) is undoubtedly a popular product for obtaining a wide range of new materials (films, granules, sponges, fibers), and the creation of polymer mixtures based on it is one of the promising and economical directions. Cellulose possesses such properties as biocompatibility, non-toxicity, biodegradability and accessibility, and its combination with polyurethane rubbers, characterized by wear resistance, oil and fuel resistance, vibration resistance, good cushioning properties, will allow to give the materials described above the characteristics, as well as elasticity, unusual for cellulose [11, 12]. Thus, the development of materials for draining oil/water emulsions using renewable, environmentally friendly and affordable raw materials is relevant.

The purpose of the work is to study the features of producing hydrophilic and oleophobic films based on cellulose and polyurethane rubber, which have improved physical and mechanical characteristics and thermal stability compared to cellulosic materials, for use them as sorbents for draining oil/water emulsions.

EXPERIMENTAL

Materials. In the work the following materials were used: microcrystalline cellulose (AvicelPH-101, Sigma-Aldrich, M_W = 60 000), polyurethane (PU) rubbers PU-8TB (M_W = 60 000), and PU-8A (M_W = 100 000), dimethylacetamide (chemically pure grade, 99.9%), anhydrous lithium chloride (chemically pure grade, storage was carried out in a dry desiccator over P_2O_5); P_2O_5 (chemically pure); $NaNO_3$ (chemically pure); K_2SO_4 (reagent); methane-naphthene oil (ρ_0 = 0.811 and 0.835 g cm^{-3}), *n*-decane (chemically pure), acetone (analytical grade), deionized water.

Preparation of cellulose and polyurethane rubber solutions. Previously, 9.33 g of dimethylacetamide and 0.67 g of LiCl were placed in a vial, stirred at a temperature of 80°C for 30 min, then weighed cellulose and PU-8TB/PU-8A with a total polymer content of 3% (of which the amount of cellulose in the solution was 20–100 wt %) were added and stirring was continued until the polymers were completely dissolved (about 10 h).

Molding of cellulose and polyurethane rubber film materials. The polymer solution was passed through a 160 Schott filter, degassed using a water-jet pump, poured into a Petri dish, coagulated, kept in a desiccator with a relative humidity of 98% (over K_2SO_4) for 12 h, washed repeatedly with distilled water, then dried at a temperature 40°C to constant weight. The film thickness was determined with a GRIFF micrometer of MKTs 25 grade (State standard GOST 6507–90 "Micrometers. Technical conditions"). It was 40–60 μm.

Structural studies. The structure of the films was studied by IR spectroscopy on an InfraLUM FT-08 apparatus (Russia) using an attachment of frustrated total internal reflection (FTIR). Before recording the spectra, the samples were kept for 24 h in a desiccator with a humidity of 66% (over a saturated $NaNO_3$ solution) at room temperature. The interpretation of IR reflection spectra was carried out using literature data on the assignment of the frequencies of functional groups in the spectra of analog compounds.

Thermogravimetric studies. The temperature stability and degradation of film samples were studied on a Q-1500D derivatograph (MOM, Hungary) with a thermocouple when heating samples in ceramic crucibles from room temperature to 1000°C in air, the temperature rise rate was 5 deg min^{-1}. The reference was calcined alumina. The weight of the samples was 102–104 mg. The curves of temperature (*T*), changes in wieght (TG), differentiated curves of changes in thermal effects (DTA), and differentiated curves of changes in weight (DTG) were recorded.

Physical and mechanical research. The strength properties of the films were determined on a ZwickiLine 5kN zwicki tensile testing machine (Germany) at a tensile speed of 1 mm min^{-1} according to GOST 14236–81 "Polymer films. Tensile test method." Samples of rectangular shape with a width of 2 mm and a length of 20 mm were used for testing. Before testing, the samples were conditioned for at least 16 h according to GOST 12423-2013 "Plastics. Conditioning and testing conditions for samples (samples)" at a temperature of 23 ± 2°C, relative humidity 60 ± 5%.

Determination of the lyophilic properties of the surface of film materials. Water absorption was determined by measuring the amount of water absorbed by the film samples, by changing the mass of the samples in desiccators with zero humidity (above P_2O_5) and 98% (above K_2SO_4) according to GOST 10315–75 "Electrical insulating materials. Methods for determining moisture resistance and water resistance."

GOST4650–2014 "Plastics. Methods for determining water absorption" regulates the determination of water absorption: the amount of sorbed water by film. Before the test, the films were dried in desiccators over P_2O_5 for 24 ± 1 h at 23 ± 2°C. After drying, the samples were removed from the desiccator and weighed after no more than 5 min. At least 8 cm^3 of water was taken per cm^2 of the surface of the sample. The prepared samples were quickly immersed in distilled water and

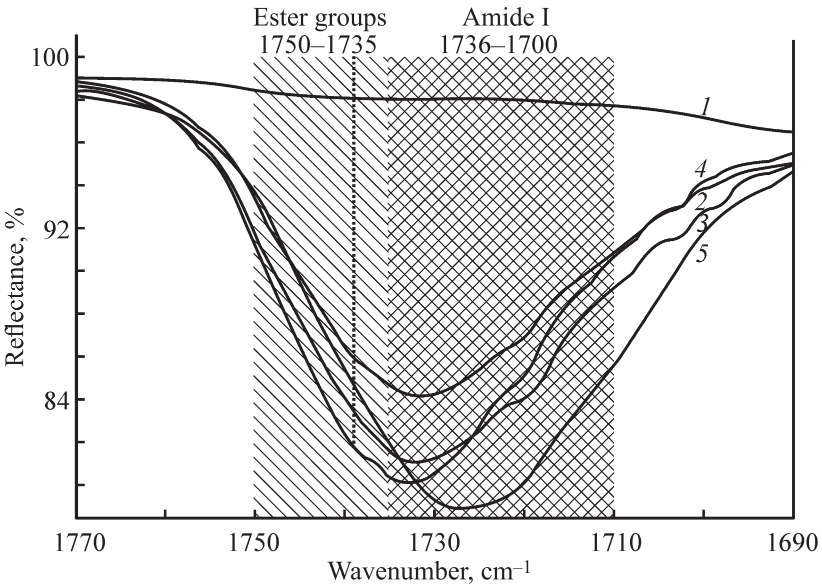


Fig. 1. IR spectra of films based on (*1*) cellulose (*2*) C/PU-8TB (5%), (*3*) C/PU-8TB (10%), (*4*) C/PU-8TB (25%), (*5*) PU-8TB.

kept at 23 ± 2°C for 24 ± 1 h, taken out every hour, wiped with a clean dry cloth or filter paper and weighed after no more than 1 min.

The determination of oil absorption was carried out similarly to the measurement of water absorption. Methane-naphthene oil ($\rho_0 = 0.811$ g cm^{-3}) was used as drained liquid with a water content of 0% measured by the Dean–Stark method according to GOST 2477–2014 “Oil and oil products. Method for determination of water content.”

The surface wetting of the synthesized films was defined on an OSA 15 EC instrument of DataPhysics company (Germany). Hydrophilic properties were evaluated by the sessile drop method [13] in a non-polar liquid medium—decane. To study the change in the contact angle with time in a decane medium, a drop of water with a volume of 10 μL was placed on the surface of each film.

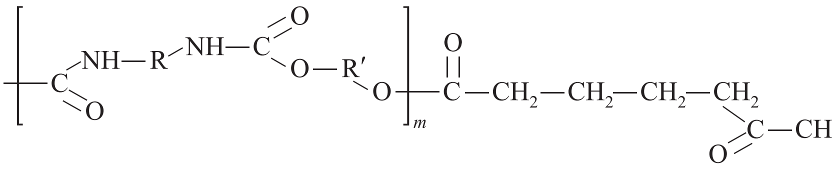
Drainage of oil. To assess the possibility of oil draining by films, samples of 1 cm^2 in area were immersed in 8 mL of methane-naphthene oil ($\rho_0 = 0.835$ g cm^{-3}) with a water content of more than 10%. The draining efficiency was estimated by IR spectroscopy using a collapsible liquid cuvette with CaF$_2$ window material and a layer thickness of 0.06 mm. The degree of water absorption from oil was determined by a decrease in the intensity of the absorption bands of hydroxyl groups observed in the regions of 3100–3600 and 1650 cm^{-1}.

RESULTS AND DISCUSSION

A necessary conditions for the use of various materials in the field of separation and drainage of oil/water emulsions are wear resistance, oil and gas resistance, elasticity, which are not typical for pure cellulose. Therefore, it is necessary to additionally use fillers or develop composite materials based on this polysaccharide and synthetic polymers, among which polyurethane rubbers can be considered as the most promising relative to their properties. Combining cellulose with polyurethanes, it is possible to obtain biomaterials that possess the wear resistance, oil and fuel resistance, and elasticity required for selective sorbents in the drainage of the oil/water emulsions.

The calculation of the hydrophilic-lipophilic balance (HLB), taking into account the ratio between hydrophilic and hydrophobic groups in the compound, was performed by the Davis method [14]. From the calculation it follows that cellulose is a hydrophilic polymer (HLB > 20), which is explained by the high content of hydroxyl groups. However, it does not

Scheme 1. The structural formula of polyurethane rubbers.



PU-8TB (R is diethylene, R^1 is propylene); PU-8A (R, R^1 are diethylene).

possess the necessary oleophobicity, which can be achieved by introducing oil and fuel resistant rubbers into the composition of the materials.

A distinctive feature of PU-8TB and PU-8A polyurethane rubbers is that their structure includes terminal carboxyl groups, which, under the conditions of dissolution of the polymer system, can interact with the hydroxyl groups of cellulose (C) (Scheme 1).

The IR spectroscopy method was used to establish the structural features of composite films (Fig. 1).

In the regions of 1750–1735 and 1736–1700 cm^{-1}, absorption bands are observed that are characteristic of C = O stretching vibrations of esters and the urethane group, respectively. Due to the close proximity of these bands in the spectrum, they overlap. In addition to the absorption bands of 1726–1734 cm^{-1}, characterizing the amide group of rubber, there is an absorption band of 1738 cm^{-1}, which is probably due to the formation of an ester bond between macromolecules as a result of the interaction of the hydroxyl groups of cellulose with the terminal carboxyl groups of polyurethane.

A study of the thermal stability of the obtained films by the method of thermogravimetry (Fig. 2) showed that the weight loss of the samples of both pure cellulose and the mixed composition in the temperature range up to 700°C goes through several stages.

At temperatures from 20 to 150°C, weight loss occurs, which is associated with the removal of unbound moisture. A further increase in temperature contributes to the destruction of hydrogen bonds, and therefore, in the temperature range 150–240°C, a change in the mass of the samples is observed, which is probably caused by the desorption of volatile compounds from the surface and volume of the samples.

The temperature at which the destruction of both samples (T_d) begins is ~240°C. In the temperature range 240–350°C, the decomposition rate of the samples is maximum (Fig. 2, curves *1, 2*). So, for cellulose, the weight loss of the sample, determined by the change in peak intensity, is 6% min^{-1}, for samples containing polyurethane rubber, 4% min^{-1}. Thus, the destruction rate of the mixed compositions is lower than that of the original cellulose.

The melting temperature of polyurethanes is rather high (not lower than 160°C) caused by the formation of hydrogen bonds between macromolecules due to polar groups [15]. When heated to a temperature above 220°C, polyurethanes begin to decompose. Based on this fact, it can be assumed that the peak in the temperature range of 350–420°C on curve *2* (Fig. 2) is associated with the interaction of cellulose and polyurethane rubber, which leads to a delay in the decomposition of the composition.

At a temperature of 380°C, the samples lose up to 60% of the initial mass, and in the case of a C/PU film, thermal degradation is slower than that of a pure cellulose film, but then (at temperatures above 380°C)

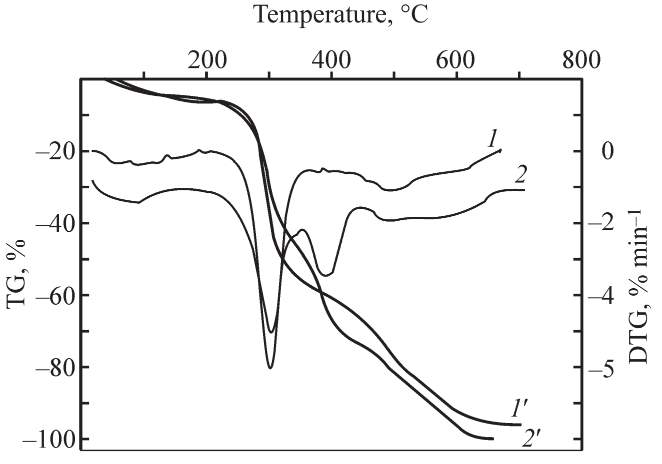


Fig. 2. Mass loss curves when heating (*1′*) cellulose films and (*2′*) C : PU = 60 : 40 wt % and differential thermogravimetric decomposition curves of (*1*) cellulose films and (*2*) C : PU = 60 : 40 wt %.

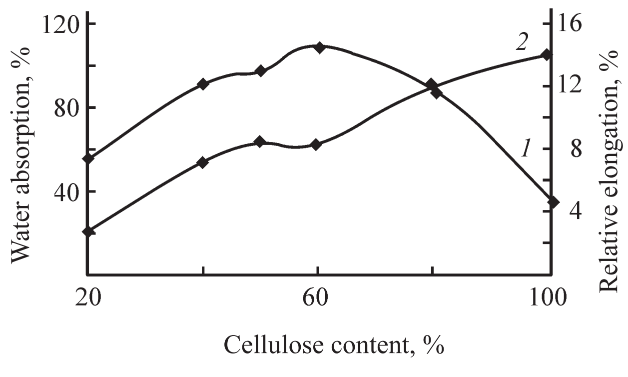


Fig. 3. Strength characteristics, (*1*) elongation, (*2*) strength, of cellulose-based films and PU-8TB.

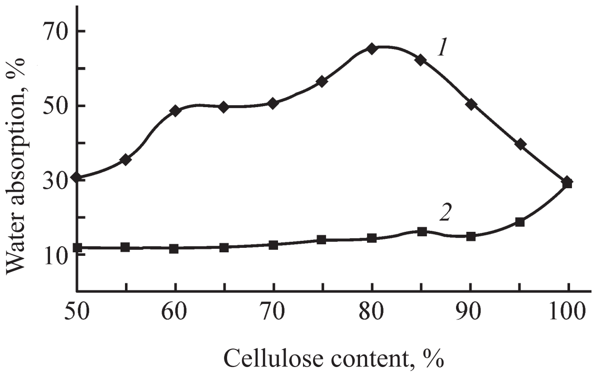


Fig. 4. Changes in water absorption vs. composition of composite films for (*1*) PU-8TB, (*2*) PU-8A.

the situation changes, and the cellulose weight loss is more than 60% occurs at a temperature of ~480°C in comparison with a mixed composition losing the same weight at ~410°C, which can be used when developing a method for the disposal of used composite materials.

A study of the physicomechanical properties (Fig. 3) of the samples showed that the strength of films based on mixtures of cellulose and polyurethane rubber decreases with increasing polyurethane content. The change in the relative elongation of the films passes through the concentration maximum. Samples with a polyurethane content of 40% have maximum elongation, and it is 3 times higher than that for a cellulose film. Such a behavior of the films is probably associated with the ordering of the film structure due to the organization of a system of hydrogen bonds [16].

When the content of polyurethane rubber is 5–30%, the relative elongation increases, and the strength decreases insignificantly, which makes this compounding more interesting for further study in order to determine the directions of practical use. An increase in the content of polyurethane rubber up to 50% or more is accompanied by a significant decrease in strength characteristics (Fig. 3).

The change in water absorption depending on the cellulose content in the film materials exhibits that mixed samples with the content of PU-8TB less than 50% have higher hydrophilic properties compared to the cellulose film, and some are able to absorb 2 times more water (Fig. 4). However, for mixed samples C/PU-8A the degree of water absorption decreases with rising amount of rubber.

To further evaluate the hydrophilic as well as oleophobic properties of the film materials, studies were conducted to found the degree of water and oil absorption. It should be noted that cellulose film samples have a rather low oil absorption value compared to fibrous cellulosic materials [17]. Mixed materials with an PU-8TB content of less than 30% not only show high oleophobic properties, but are also able to absorb more

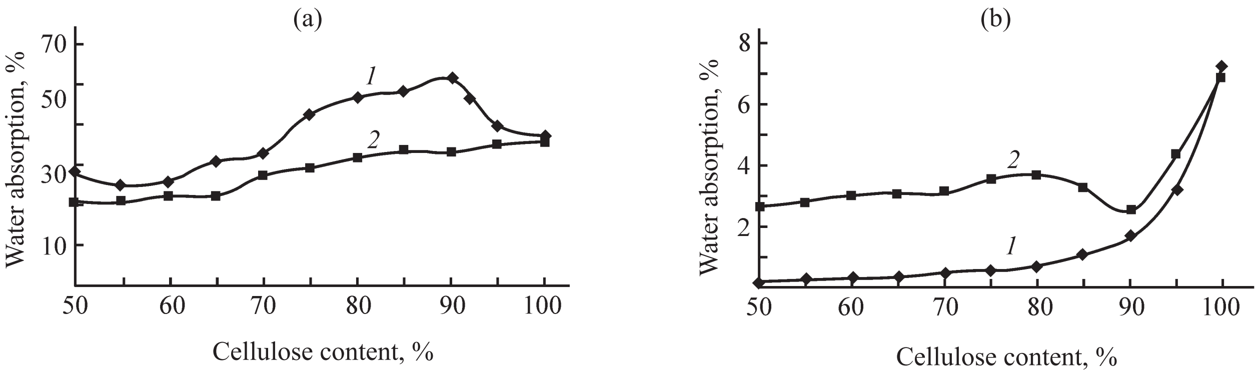


Fig. 5. Change in (a) water and (b) oil absorption vs. composition of composite films for (*1*) PU-8TB, (*2*) PU-8A.

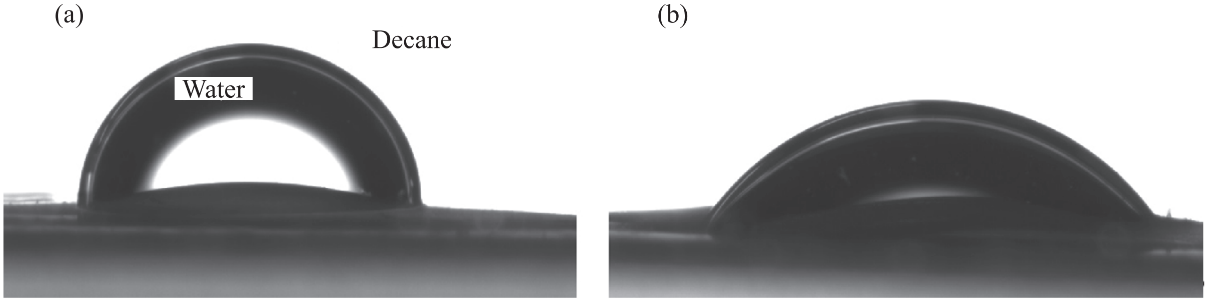


Fig. 6. A drop of water on the surface of a cellulose–polyurethane film in a decane medium. (a) At the initial time, (b) in equilibrium.

water compared to cellulose film (Fig. 5a). For mixed samples C/PU-8A, the degree of water absorption decreases with increasing amount of rubber.

Oil absorption of mixed compositions with both PU-8TB and PU-8A decreases with an increase in the proportion of synthetic polymer (Fig. 5b). Nevertheless, films containing PU-8A absorb a greater amount of petroleum hydrocarbons, in contrast to films of the composition C/PU-8TB.

To assess the possibility of interaction of mixed films with water in oil, dynamic studies of the behavior of its droplets on the surface of cellulose and composite samples were carried out.

For samples C/PU-8TB (Fig. 6), the change in the contact angle of a water drop in a non-polar liquid medium (*n*-decane) identical to oil correlates well with data on water absorption. The best hydrophilicity and water absorption are characterized by samples with rubber content up to 25%. The contact angles of water droplets in equilibrium are 3–15° lower than that of a cellulose film (Fig. 7).

At the same time, the introduction of PU-8A into the composition does not lead to an increase in the hydrophilic properties of film materials (Fig. 8). Only with the addition of 5% rubber the contact angle in equilibrium becomes smaller than that of the original cellulose film.

As a result of studying the lyophilic properties of the surface of mixed films, it was revealed that materials based on cellulose and PU-8TB possess the best hydrophilic and oleophobic properties. Based on this fact, the optimal formulation of the composition for draining oil containing 90% cellulose and 10% PU-8TB was determined.

The results of IR spectroscopy (Fig. 9) show that the selected mixed films can remove a significant amount of

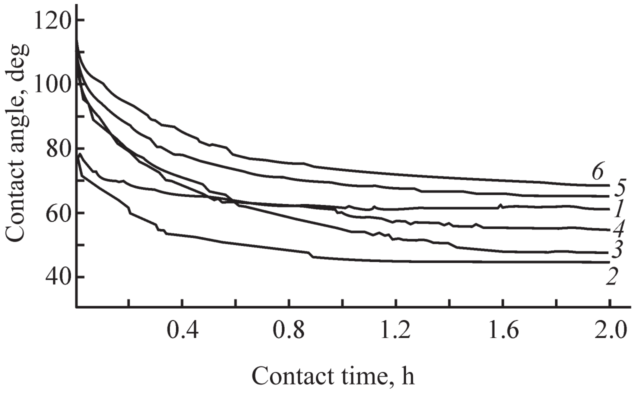


Fig. 7. Contact angle vs. contact time of a water drop with the surface of the films in the decane medium for samples C/PU-8TB. (*1*) cellulose; (*2*) C/PU-8TB (5%), (*3*) C/PU-8TB (10%), (*4*) C/PU-8TB (20%), (*5*) C/PU-8TB (35%), (*6*) C/PU-8TB (40%).

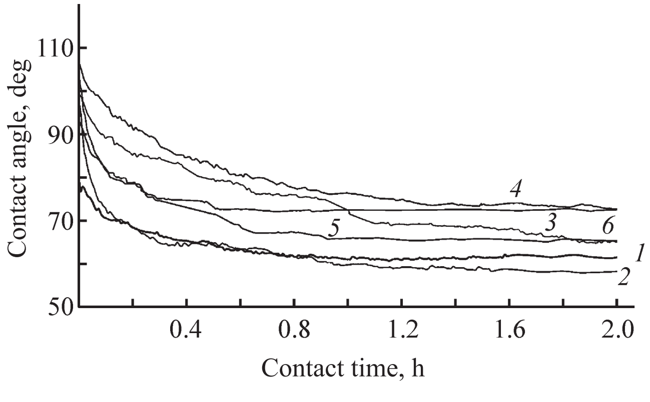


Fig. 8. Contact angle vs. contact time of a water drop with the surface of the films in the decane medium for samples C/PU-8A. (*1*) cellulose; (*2*) C/PU-8A (5%), (*3*) C/PU-8A (10%), (*4*) C/PU-8A (20%), (*5*) C/PU-8A (25%), (*6*) C/PU-8A (50%).

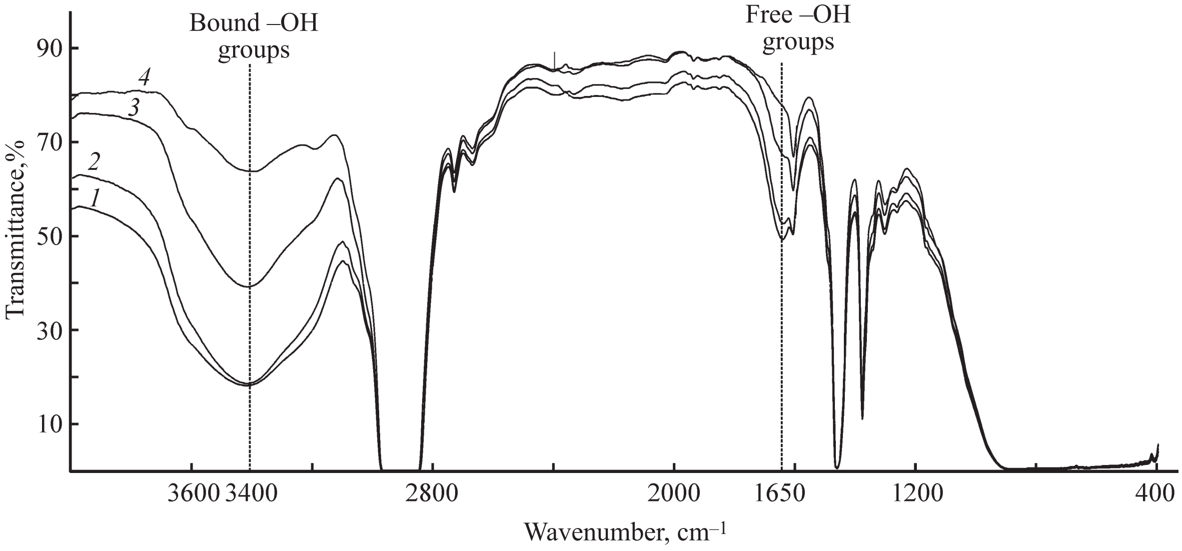


Fig. 9. IR spectra of oil: (*1*) origin and after drying for (*2*) 6 h, (*3*) a day, (*4*) 3 days.

water from oil, which is confirmed by a decrease in the intensity of the absorption bands of bound and free –OH groups at 3400 and 1650 cm^{-1}.

CONCLUSIONS

According with the results of the studies, it can be concluded that mixed film materials based on cellulose with a polyurethane content <40% have the best hydrophilic, oleophobic, and physico-mechanical properties in comparison with cellulose films. The chemical interaction of the hydroxyl groups of cellulose with the carboxyl groups of polyurethane rubber was confirmed by IR spectroscopy. The described features of the thermal properties of mixed compositions in the future will allow regenerations of materials from absorbed water without destroying them. Thus, the set of properties obtained indicates the possibility of using materials based on cellulose and polyurethane rubber as eco-friendly sorbents and membranes for draining water/oil emulsions.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

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