

Perspectives of use of nanocellulose in oil and gas industry

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Abstract

The article reviews basic properties of nanocellulose, indicates sources of raw materials and peculiarities of its formation. It has been found out that the main factors that determine the size and structure of nanocellulose is the raw material, the conditions of treatment and methods of generation of nanoscale crystals.

It has been demonstrated that cellulose nanoparticles can be used as environmentally friendly additives for water-based drilling fluids with predetermined rheological and filtration properties, as well as corresponding thermal resistance, which increases the efficiency of drilling technology.

It has been noted that the nanocomposite material "cellulose – polyethylene" can be raw material for the production of a new generation of plastic pipes with better strength characteristics and high resistance to slow and rapid crack propagation if compared to traditional materials.

Keywords: *drilling fluids, nanocellulose, plastic pipes, polimer composite, rheological properties.*

During the extraction, transportation and processing of oil and gas, technology must be sophisticated, equipment must be reliable and the materials being used should have predefined properties, such as high reliability, thermal, corrosion and chemical resistance [1, 2]. Composite materials are the best to meet these requirements. Composites provide constructions with specific characteristics, especially if they are combined with other materials [3, 4].

Plastics are flexible, chemically resistant materials with low thermal conductivity, excellent dielectric and optical properties, high corrosion resistance, the ability to absorb and extinguish vibration. This explains their widespread use in the oil and gas sector. Today, one of the promising areas of research is the development of principles of obtaining and study of the properties of polymer composites and nanocomposites [5].

Modification of polymers, including structural and chemical modification, using reactive compounds is one of the effective methods of regulating their structure and properties. Thanks to them, it is possible to create composites that combine the beneficial properties of polymers and fillers and are plastic. This combination significantly expands the scope of use of these materials.

At the same time, the use of plastics derived from renewable raw materials capable of biodegradation is an actual problem of modern materials study, related to both the needs of new functional polymers, and the problems of limited oil and gas reserves, reducing CO₂ emissions, disposal of used polymer materials that pollute the environment [6].

Production and properties of nanocellulose

Cellulose (fiber) is the most common natural biological polymer [7]. It is located in the cells of plants and bacteria. Cellulose chains are built from the remnants of β-glucose and have a linear structure, and all the OH groups are only outside of the circuit (Fig. 1). Due to this hydrogen bonds are emerging between macromolecules of cellulose, which give substance stiffness and make it insoluble in water.

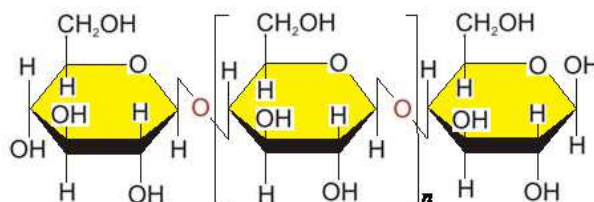


Figure 1 – Structural formula of cellulose

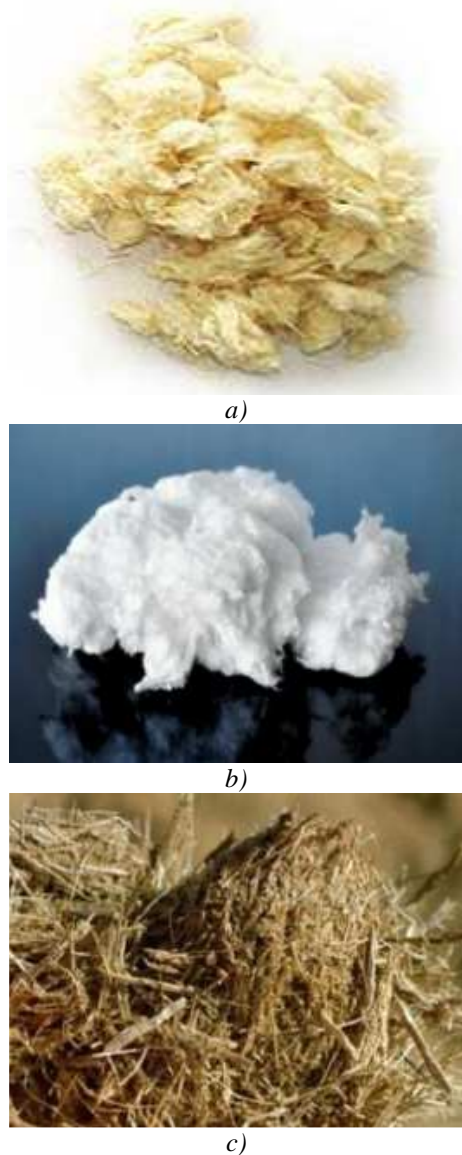
Currently, cellulosic materials are widely used for a variety of nanostructures, nanocrystals, nanofibers and nanocomposites. Nanocomposites can be fully formed from cellulose (matrix fibers are longer, and the filler is cellulose nanocrystals). They may contain nanoparticles

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of metals and semiconductors, have an organic matrix from bacterial or chemically modified cellulose. In composite materials, cellulose is also combined with synthetic polymers [8].

The source of raw material for cellulose is timber, which is a combination of cellulosic fibers held together by lignin matrix – another natural polymer that is easily decomposed and removed. The process of production of cellulose is to remove lignin and obtain an aqueous suspension of cellulose fibers. Typical wood pulp layer (Fig. 2) is tens of microns wide and about a millimeter in length. Cultivated crops, such as cotton and sugar beet pulp could serve as alternative raw materials in the production of cellulose [8].



a – timber cellulose; b – cotton cellulose; c – sugar beet pulp cellulose

Figure 2 – Fibrous semiproducts for cellulose production

If you break cellulose fibers to nanofibrils that are about a thousand times smaller than the fibers themselves, you can get a three-dimensional grid of long unbranched filaments of cellulose molecules,

which are connected via hydrogen bonds. Hydrogen bonds between molecules of cellulose are strong enough to provide strength and rigidity of cellulose nanocrystals. These nanofibrils form sections, in which the molecules are arranged, and the cellulose chains are parallel.

In some of these areas there are few disordered nanofibrils, separated by amorphous secluded area. These individual nanocrystals can be easily removed by dissolving amorphous areas with strong acids.

The length of the material, separated from wood, is usually a fraction of a micron. It is of a square section with sides of a few nanometers. Its density is low – 1.6 g/sm³, but it has high strength: modulus of elasticity is 150 GPa and tensile strength is up to 10 GPa (Table 1) [9].

Table 1 – Properties of different materials

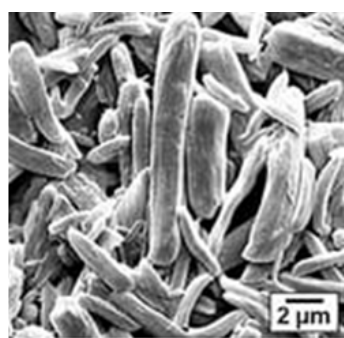
Material	Modulus of elasticity, GPa	Tensile strength, GPa
Nanocellulose	150	9,5
Kevlar 49	125	3,5
Carbon fiber	150	3,5
Carbon nanotubes	300	20
Stainless steel	200	0,5
Oak timber	10	0,1

As the table shows, only carbon nanotubes have a greater strength if compared to cellulosic nanocrystals. Stainless steel can be only compared with traditional materials. Nanocellulose crystals are stronger and tougher than kevlar. And one can get products of higher strength but less weight. Besides a large number of hydroxyl groups on the surface of nanocellulose allows various chemical modifications that let us get materials with desired properties and use in different spheres of oil and gas industry.

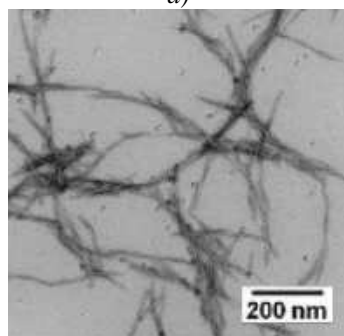
The methods of manufacturing of nanocellulose have been scientifically investigated since 1960s and in the last decade it has been produced on an industrial scale. The technologies of nanocellulose production have been developed, taking into account the data obtained from studies of properties of microcrystalline cellulose. Microcrystalline cellulose is a product of the chemical degradation of cellulose, which has a high purity and high content of ordered cellulose with crystalline orientation of macromolecules.

The main difference between the nano- and microcrystalline cellulose (Fig. 3) is the size of highly crystalline aggregates and the degree of crystallinity, which in its turn causes the appearance of their specific properties. Dimensions of nanocellulose fibers vary widely. Cellulose nanocrystals are core with a length of 50–2000 nm and a diameter of 3–40 nm. The main factors that determine the size and structure of nanocellulose is the raw material, processing conditions and methods for production of nanoscale crystals [10].

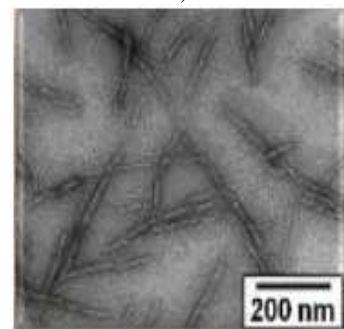
Creating composites, containing fillers of nanosized dispersion levels, is a new and promising direction in the development of materials science. One of the promising options in this area is the use of natural



a)



b)



c)

a – microcrystalline cellulose; b – nanofibril cellulose;
c – nanocrystalline cellulose

Figure 3 – Electronic photos of samples

polysaccharides, including cellulose, with a distinct fibrillar structure, to improve the physical and mechanical properties of various polymers, accelerate their biodegradation after the end of use, reduce CO₂ emissions in the process of production, processing and exploitation of polymeric materials with specified properties. Limiting factors in the creation of composites of this type are dispersing of polysaccharide fibrils to nanosized level and retention of their core configuration with the correct ratio of length to diameter [11].

Use of nanocellulose in hydrocarbons production

In the process of well drilling in oil and gas fields it is necessary to make a durable, sturdy and insulated channel, connecting the productive horizon with the surface. Drilling fluids are crucial in wells drilling. It must be mentioned that not only the effectiveness of drilling but also the life of a well depend on the ability of drilling fluids to provide for its functions in different geological and technical conditions. Therefore, it is preferable to use drilling fluids, containing clean

ecological biodegradable materials instead of chemicals that are harmful for personnel and environment [12].

To improve the efficiency of drilling fluids and address the growing problems in the oil and natural gas production, micro- and nanoparticles are used with increasing frequency [13, 14]. The results of studies [15, 16] have shown that nanoparticles of cellulose can be used as ecologically clean biodegradable additives for water-based drilling fluids with specified rheological and filtration properties and corresponding thermal stability.

The particles of cellulose nanocrystals can be used as an additive to cement slurry. It is known that set cement ring is impermeable to gas as a pillar of suspension being injected. However, there is the phase between the two states, which lasts only a few hours during which the cement is losing the properties of the liquid, but not yet is a solid impermeable substance. migration of gases can occur during this period. Adding of nanocellulose particles can provide hermetic insulation of cement slurry during the whole period of cement slurry setting [15, 17].

One of the new and promising areas with a high potential for improving deepwater drilling operations safety while maintaining profitability is to use aerogel as an effective insulated layer in marine exploration and extraction of oil and gas [18].

Aerogel is a special highly porous nanostructured material with unique properties: low density (0.004–0.5 g/sm³), a large specific surface area (600–1000 m²/g) with a pore size of about several nanometers, low thermal conductivity (0.02 W/mK). The properties of this material are determined by the synthesis conditions. By changing these conditions, you can get the materials with the necessary mechanical properties.

Sound isolation is the main condition of underwater oil and gas operations, as there is a need for a thermal barrier between streams of transported hydrocarbons and sea water. It is important to maintain the temperature of crude oil or natural gas flowing through pipes within the range of 30–50 °C, which prevents flow restriction or pipe clogging due to hydrate formation or wax delay in the transportation of hydrocarbons to the sea surface. In [19, 20] it has been reported that the use of clean and strong aerogels has significant potential to improve the insulation of deepwater oil and gas pipelines by reducing the cost of its installation, increasing the flow of hydrocarbons, increasing resistance to deep-sea pressure, reduction of steel pipeline designs and reliable insulation.

Cellulose can be perspective polymer for the production of polymer aerogels on biological basis because of its biodegradability at the end of the operation period, availability, biocompatibility, and the ability for chemical modification [21]. The porous aerogel is notable for elasticity in spite of conventional aerosols.

In the course of research it has been found out that aerogel from cellulose readily absorbs oil, so floating pads with cellulose aerogel can collect spilled oil from the water surface, and their ability to absorb is about 100 times greater than its weight, and floating pads after

the removal of product and washing can be re-used [22, 23].

During the search, exploration and development of oil and gas fields different technological transport is used, such as logging platforms, geophysical exploration laboratories, seismic vibration exploration unit, units for maintenance and major repairs of oil and gas wells, mobile compressor stations, etc [24].

All the transport and attachable equipment (rigging) are set in motion by gasoline and diesel engines of vehicles through transmission elements, including power take off devices and gearboxes, reduction gear boxes, chain transmission shafts with bearing units etc. To ensure reliable operation of engines and transmission units, high performance oils and high-value gasoline and diesel fuels and gas, compressed natural gas and LNG are used.

Currently, the researchers are working to create new materials in order to enhance the reliability and reduce the weight of vehicles. Thus, according to the authors [25], reduction of vehicle weight by 10 % can reduce fuel consumption by 6–8 %. Polymer composites, based on nanocellulose due to lower density help to reduce weight and basically meet the requirements of the automotive industry, and in some cases are even much better [26].

Reducing the cost of motor fuel in the operation of oil and gas process transport is an important factor of energy saving and environmental protection. It is particularly important to solve this problem due to the forecasted decrease in production of oil, gas and motor fuels, particularly fuels for transporting and driving of attachment equipment (rigging) of oil and gas technological transport.

Several car producers, including Ford conduct a stable policy aimed at use of nanocellulose. They replace with it traditional plastic materials such as talc and glass fiber, that except for technical and economic advantages, promotes improvement of ecological situation [27].

In terms of analysis and design of manufacturing operations in vehicles production, as well as understanding of the relationship between structure and properties of polymerstheir rheological properties are of a great importance [28]. However, despite its importance, the rheological properties of nano-composites based on cellulose are rarely investigated and up to date little studied. Because such studies and their implementation will effectively maintain and increase the use of nanocellulose composites in various fields of oil and gas process transport.

Nanocellulose use pipeline systems

The use of polyethylene pipes may help us to increase reliability of oil field piping systems and reduce energy and labor costs in the construction of pipelines. Currently in our country and abroad quite rich experience in the use of plastic piping in gas distribution systems has been accumulated. However, the issue of reliability, cost of work and increase of service life

make providers to introduce innovative methods of laying pipelines and use new materials.

Innovations in this sphere include primarily trenchless laying techniques in the construction of new plastic and replacement or repair of metal pipelines damaged by corrosion [29]. Methods of trenchless laying of pipelines are alternatives to the traditional trench method to overcome the obstacles encountered on the path of the pipeline (rivers, roads, dams, etc.) without violation of their functioning. Trenchless laying of pipelines is a high-tech process that is carried out, using modern equipment.

Laying of plastic pipelines by trenchless method can be performed using different technologies, such as soil piercing, horizontal directional drilling and trenchless plowing. The difference between these technologies does not affect the quality of performed works. It is caused only by natural and other conditions such as composition and density of soil, remoteness of communications and diameter of pipes being laid.

One of the most effective methods for replacement and modernization of gas pipelines that has served its time is "berstlayning". It is a method that involves the destruction of the old, worn-out or damaged pipes and laying new in its place. Old pipes are destroyed by powerful units with knives, moving along the pipeline. Fragments are pressed into soil with an expander. Then a new pipe of a larger diameter is being put into this space, which can significantly increase the capacity of the new pipeline.

The fragments of the old metal pipeline remain in the soil. During installation and maintenance works they can contact the outer wall of the new pipeline. Therefore, a new tube should be made from material with high resistance to external influences.

Experimental data [30] indicate that the introduction of cellulose nanoparticles in various synthetic polymers, especially polyethylene, help to improve a number of performance characteristics such as shear modulus, strength, heat resistance, hygroscopicity, gas and air permeability, and many others. Moreover it is enough to enter up to 10% of cellulose nanoparticles.

Thus, the effectiveness of innovative construction and renovation of polyethylene pipelines depends on the possibilities of using pipes made from new generation materials. Polyethylene nanocellulose composites are rather promising in this regards as they possess appropriate performance characteristics: high resistance to point loads and high resistance to slow and rapid crack propagation. The use of this composite material in the form of single-layer and multi-layer pipes will help to increase the pressure in the system and the productivity of the pipeline in general. Regarding the construction of plastic pipelines in the near future there must be a new approach, focused on the application of trenchless technologies and use of pipes made from polymers of new generation, which in its turn requires the development of evidence-based strategies of development of this direction and improvement of the regulatory framework of works to be implemented.

Conclusions

Creation and use of composite materials which contain nanosized fillers of dispersion, is a new and promising area of oil and gas sector development. Adding nanoparticles of cellulose improves the efficiency of drilling fluids and cementing compositions and the use of aerogels containing cellulose increases resistance to deep-sea pressure, improves isolation and heat insulation of deepwater oil and gas pipelines, reduces steel content in piping designs and cost of installation.

However, despite its relevance chemical, structural and mechanical properties of cellulose-based composite materials have been insufficiently studied. Also there is a need to study the properties and characteristics of different types of nanocellulose – nanocrystals nanofibril, bacterial cellulose and mechanisms of their interaction with other materials. This research and implementation of recommendations at the different stages of hydrocarbons production and transportation will increase the efficiency of enterprises, ensure their competitiveness on the domestic and global markets and improve the ecological situation.

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Перспективи використання наноцелюлози в нафтовій і газовій промисловості

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Розглянуто основні властивості наноцелюлози, вказано джерела сировини та особливості процесу її утворення. Встановлено, що основними чинниками, які визначають розмір і структуру наноцелюлози, є вихідна сировина, умови її оброблення і методи отримання нанорозмірних кристалів.

Показано, що наночастинки целюлози можуть бути використані у вигляді екологічно чистих добавок для отримання бурових розчинів на водній основі із заданими реологічними та фільтраційними властивостями, а також відповідною термостійкістю, що підвищує ефективність технологій буріння.

Відзначено, що нанокомпозиційний матеріал “целюлоза – поліетилен” може стати сировиною нового покоління для виробництва пластмасових труб з кращими показниками міцності та підвищеною стійкістю до повільного та швидкого поширення тріщин в порівнянні з традиційними матеріалами.

Ключові слова: *бурові розчини, наноцелюлоза, пластмасові труби, полімерні композити, реологічні властивості.*