# Improvement of the Quality of Water Purification from Hydrocarbons Using the Fibers from Recycled Thermoplastics

**O V Galtseva[1], S V Bordunov[2], N M Natalinova[1] and S V Mazikov[3]**

[1]Associate Professor, National Research Tomsk Polytechnic University, Tomsk, Russia
[2]Superviser, Public Corporation Scientific - Innovation Enterprise “Echteh”, Tomsk, Russia
[3]Student, National Research Tomsk Polytechnic University, Tomsk, Russia

E-mail: rabota2013tpu@mail.ru

**Abstract.** Adsorption properties of the polymer fibers are studied. It is shown that polypropylene fiber can be successfully applied for oil spill response for filtration purification of water from hydrocarbons. Polypropylene fibers from waste polymers have higher characteristics of adsorption capacity and degree of purification of water than commercially available fiber sipron.

## 1. Introduction

At the present time almost all of the extracted oil passes from production sites to consumers through a developed system of field and main pipelines, which because of this are the zone of high ecological danger. Since 100% reliability of any functioning system is almost unattainable, the possibility of an emergency with appropriate consequences always exists. An actual problem for the whole world is fight against spills of oil and oil products at accidents. At oil spill the main danger should be considered the spread of oil on big squares on a surface of the soil and water leading to violations of ecological balance of territories and doing impossible normal functioning of biological systems for a long time. The spillage of oil and oil products in the aquatic environment is extremely dangerous because it may be accompanied by spreading of them over a distance of hundreds of kilometers from the scene of the accident.

Number of consecutive technological operations is applied upon liquidation of oil spills on the water surface: localization of the oil slick by floating booms, pumping of main mass of oil by the high-performance mechanical or vacuum skimmers, equipped by separators for separation of oil from water and use of oil for designated purpose. A layer of oil with thickness up to 1 – 2 mm remains on the water surface as a result of this operation. The final purification of the water surface is carried out by different dispersed oil-absorbing materials (OAM). The first task is usually successfully is solved, but daunting task is the collecting of thin oil films (especially, iridescent films) with thickness comparable with wavelength of the visible spectrum of daylight. The use of skimmers with external source of energy is difficult and often impossible, at the oil spills in wetlands and on areas with difficult relief.

Therefore there are two possible ways: microbiological recultivation and collecting of oil by oil-absorbing materials (sorbents).

Paper describes [1–4] the experience of application of various sorbents which used to collect of spilled oil in the pipe transport. Fibrous materials from thermoplastic materials are the most preferred with the ratio "price of adsorbent/weight of collected oil". Due to their high strength, resistance to high temperatures and corrosive influences the fibrous polymeric fibers are increasingly replacing materials from natural fibres in the industry. The technology for producing fibers from thermoplastic processing waste was developed and it is cheaper by 1.5 – 2 times than the fibers received from primary raw materials [5, 6]. These fibers can be used in the processes of separating of the methane-butane fraction from the natural gas before transport [6] and as oil-absorbing materials at liquidation of emergency floods of oil and oil products and in processes of filtration purification of oil- containing water.

## 2. Experimental

Further the main characteristics of the fibers obtained by the proposed technology are provided [5, 6]. Fibers based on polypropylene (PP) are resistant in mineral and organic acids, alkalis and they have an upper working temperature about 95 $^0$C. Fibers of polyethylene terephthalate (PE TP) with an operating temperature of 130-150 $^0$C are exposed to alkalis. Decrease of temperature border of use of received fibers is caused by partial destruction of polymers at their repeated thermal processing and decrease of their molecular weight. According to the derivatographic analysis the losses of mass of commodity granulated polypropylene are noted at 255 $^0$C, and loss of weight of 0.3% is recorded at 200 $^0$C for fiber from secondary polypropylene of the same brand. Commodity PE TP begins to lose weight at 350 $^0$C, and the fiber obtained from fleck of PE TP (bottles), loses 0.5% of mass already at 250 $^0$C.

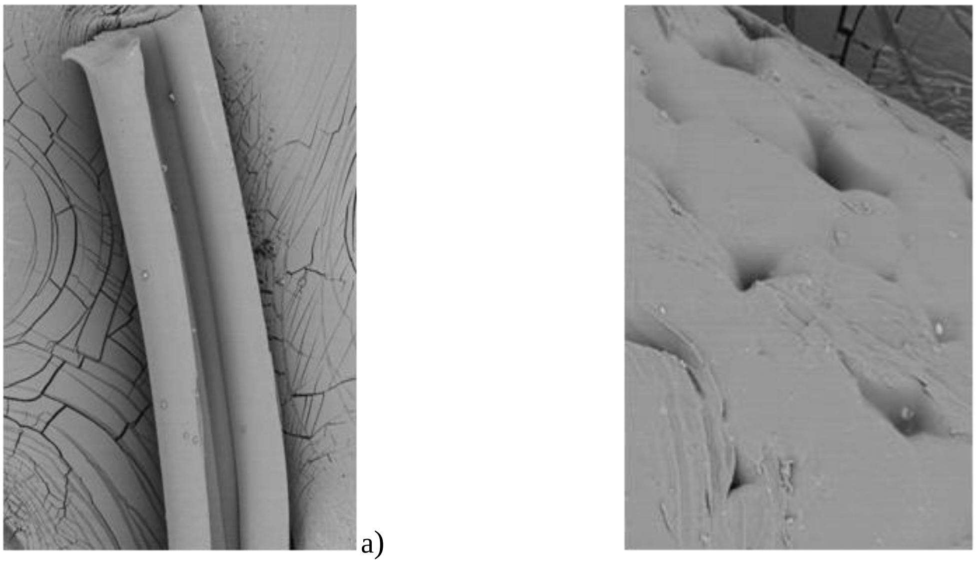
Table 1 shows the modes for producing of fibers from recycled thermoplastics. Research of possibility of recycling PP, PE, polystyrene (PS), PE TP and polyvinyl chloride (PVC) into fibrous materials by technology [5] shows the following.

**Table 1**. The recommended temperature of recycling thermoplastics into fibers by technology [5, 6].

| Initial raw material | Processing temperature, $^0$C | Diameter of resulting fibers (depending on the modes of processing temperature and rotation speed of reactor), μm |
|---|---|---|
| PP of any brands | 220–320 | 0.1–200 |
| PE of any brands | 280–320 | 0.1–250 |
| PS of any brands | 180–190 | 1.0–300 |
| PE TP – bottles | 280–290 | 0.1–300 |
| PP + PS (5-30%) | 280–290 | 20–400 |

PP and PE TP are processed into the fiber more easily and practically without losses. The strength of fibers made from individual PP and PE TP is sufficient for use as filter nozzles in filters for water and air purification and for the production of nonwovens. The optimum processing temperature of PP is in the range 250-310 $^0$C. In the temperature range 160 - 250 $^0$C melt viscosity of PP is high and it does not allow to receive the fiber even at the speed of rotation of reactor of 1400 rpm. The melt of PE TP has a lower viscosity than the melt of PP, therefore, it is possible to produce fibers at 275-290 $^0$C, i.e. it is at the temperature which higher on 5-15 $^0$C than its melting temperature. Inevitable small additions of PE in the form of stoppers and rims from the stoppers on the bottles from PE TP almost don't influence on the temperature mode of processing of recycled PE TP into the fiber at the recycling of bottles. It has a positive effect on the mechanical characteristics of the fibers of PE TP because they carry out function of a plasticizer. Additives of secondary PE (up to 30%) into secondary PP behave similarly without influencing on temperature mode of processing of PP into fiber.

Figure 1 shows photos of the fibers obtained in [7, 8]. Investigation of the surface of fibers on the electron microscope at a magnification of 1000 times in the Nano-Center of TPU (figure 1) show that only fibers with diameter less than 30 μm have in the cross section of the circle and smooth the surface. More complicated geometry of fibers in the cross section is observed with the increase of the diameter of the resulting fibers. For example, the shape of tape twisted from two parties on width is associated with lateral pressure on the melt in spinnerets which are directed oppositely to the rotation and non-uniform expansion of a jet of the melt outside the reactor. In addition, cracks and cavities appear on the surface of fibers with a diameter more than 100 μm, which explains the decrease in their strength.



a) b)

**Figure 1**. Photos of samples of fibers obtained on installation [8], equipped with reactor with r = 125 mm and 156 dies: a – diameter is 100 μm, magnification is 200 times, b – diameter is 100 μm, magnification is 1000 times, cavities are 1–5 μm.

The wettability of the material by the adsorbed liquid determines the value of the regional angle of wetting. It is one of the main characteristics of adsorbent determining its absorbing ability by this liquid. Besides, adsorbents must have the low cost, availability and rather high mechanical strength. Polymer fibers meet these conditions.

Adsorption on the oil-absorbing materials from polymeric fibers proceeds by the principle of capillary condensation. This phenomenon is due to the influence of the surface curvature of the liquid meniscus on the vapor pressure of the substance over it. The relationship between vapor pressure above the meniscus and above the flat surface of the liquid is established by the Thompson's equation (equation 1):

$$p_0 / p = exp(2\sigma \cdot V_0 \cdot cos\theta / R \cdot T \cdot r), \quad (1)$$

where $\sigma$ is a surface tension of liquid; $V_0$ is a molar volume of liquid; $r$ is radius of capillary; $cos\theta$ is a regional angle of wetting of surface of material by liquid.

Analysis of the Thompson's equation shows that capillary condensation is determined by the wetting of the capillary walls by liquid and its surface tension. The radius of the capillary depends on the porosity and the diameter of the fibers of the filter material.

The wetting of surface of polymer material by liquid was determined by direct measurement of drop under a microscope. The surface tension was determined by the method of separation of the ring from the liquid. Thin film of polymer from fusion is pre-applied on a ring. Measurement of regional angles of wetting showed that the organic compounds **(**hydrocarbons of normal structure, aromatic (benzene, toluene, xylene), alcohols of normal structure**)** spread on a material surface**,** i.e. $cos\theta$ is close to 1.

Table 2 gives the experimental data about wettability of polymeric materials by water. Table 3 gives the data about surface tension of hydrocarbons on a surface of polymers.

**Table 2**. Angle of wetting and surface tension on border “water – polymer”.

| Material | $cos\theta$ | $\theta$, $^0$ | $\sigma$, mN/m |
|---|---|---|---|
| Polyethylene (PE) | 0.670103 | 47.925 | 68.715 |
| Polypropylene (PP) | 0.324324 | 71.075 | 66.533 |
| Polyethylene terephthalate (PE TP) | 0.724138 | 43.602 | 56.717 |

From the table 3 it is seen that the polypropylene is a hydrophobic material. Accordingly, polypropylene fiber preferably used to collect oil from a water surface, as polypropylene density is 0.9 – 0.91 g/cm$^3$ and it is lower than the density of water. PE is more hydrophobic than PP, but fibers from recycled PE TP have less mechanical strength than the fibers of recycled PP.

**Table 3**. Surface tension of hydrocarbons on a surface of polymers

| Hydrocarbon | Polyethylene (PE) | Polypropylene (PP) | Polyethylene terephthalate (PE TP) |
|---|---|---|---|
| $C_xH_{2x+2}$, $X^{/}= 3 \div 7$ | 0.775x +24.455 | 0.7606x+22.79 | 0.6602x+26.407 |
| Benzene, toluene | 1.6361x+29.267 | 2.7268x+22.723 | 1.6361x+28.359 |
| Alcohols: $C_2H_5OH$, $C_3H_7OH$ | 1.09007x+29.449 | 1.2271x+30.904 | 1.2271x+31.994 |

where $X^{/}$ – number of carbon atoms in hydrocarbon molecule.

The data of table 3 also confirm that the polypropylene is a good material for the production of fibrous oil-absorbing materials not only for collecting oil and oil products from water surface, but also for use in the processes of filtration purification of water from oil products.

## 3. Results and considerations

Fiber with an average diameter of 70 μm was used in experiments for determination of oil-absorbing characteristics of polypropylene fiber; it was obtained by technology [4] from waste polypropylene grades of 21030 – 16 ÷ 21060 – 16. In the experiments the fiber density of samples (in free blow) was 150 ÷ 160 kg/m$^3$ and the porosity was 84 ÷ 86%.

The absorption capacity of the fiber samples for oil and oil products was determined by the gravimetric method according to the method of SShZhI–1202–96 of Institute of Petroleum of Chemistry Russian Academy of Sciences, Siberian Branch, Tomsk, Russia. Preweighed sample of the fiber was placed on a water surface with a layer of oil and oil products thickness with 3 ÷ 6 mm.

Then the sample with oil products was weighed, centrifuged at a factor of division 100 ± 3, again weighed and placed in capacity with oil products and water up to 50 times.

From table 4 it can be seen that the fibers with a small diameter have a greater sorption capacity. It is caused by surface and capillary forces of holding of hydrocarbons, which increase with decreasing of fiber diameter of the sorbent and the size of the pores between the fibers.

**Table 4**. Dependence of mass of absorbed oil from diameter of polypropylene fiber.

| Type of hydrocarbons | Diameter of fibers, μm | Specific surface, m$^2$/g | Sorption capacity, g/g | Porosity, % |
|---|---|---|---|---|
| Collecting West Siberian Oil | 70 | 0.057 | 4.03 | 87 |
| Collecting West Siberian Oil | 56 | 0.071 | 4.83 | 83.5 |
| Collecting West Siberian Oil | 42 | 0.094 | 9.3 | 80 |
| Diesel fuel | 70 | 0.057 | 4.01 | 87 |
| Diesel fuel | 56 | 0.071 | 5.5 | 83.5 |
| Diesel fuel | 42 | 0.094 | 9.6 | 80 |
| The aviation kerosene | 70 | 0.057 | 2.3 | 87 |
| The aviation kerosene | 56 | 0.071 | 5.6 | 83.5 |
| The aviation kerosene | 42 | 0.094 | 5.3 | 80 |

Table 5 presents the comparative data of filtration purification of water from oil by the fibers obtained by technology [4] from waste of polypropylene and fibers which were let out industrially such as sipron, which are widely used for filtration purification of water. The average diameter of the fibers of both types used in the experiment was 40 μm. Collecting West Siberian Oil was poured in water and an emulsion was prepared by multiple shaking of the container before disappearing of visible oil stains on the surface. The concentration of oil in water was 40 mg/l is the standard concentration of oil in water, which taken as a basis for designing of treatment facilities, for example, for carwashes. The filtration was finished at a fixed initial rate of reduction of gravity filtration on 10%, and in that moment the concentration of oil in the filtrate begun to rise sharply.

From the data presented in table 5 it is seen that the obtained fibers of polypropylene are more effective than sipron for purify the water from emulsified oil in mode of the gravity filtration.

**Table 5**. Results of filtration of mixture “water-oil” on polypropylene fiber and sipron.

| Indicator | Fiber PP | Sipron |
|---|---|---|
| Density of fibers in column [kg /m$^3$] | 158 | 168 |
| Volume of emulsion passed through the column ([m$^3$/ kg] of fiber) | 837 | 236 |
| Gravity filtration rate at the start of process [m/hour] | 97.0 | 95.5 |
| Sorption capacity for oil ([kg] on 1 [kg] of sorbent) | 3.57 | 0.53 |
| Residual concentration of oil in the filtrate [mg/l] | 0.45 ÷ 0.55 | 0.7 ÷ 1.8 |

## 4. Summary

It is established that polypropylene fiber with the greatest efficiency can be used as oil - absorbing materials during liquidation of emergency floods of oil and oil products on the surface of the water. It is preferable to use a fiber with a diameter of 40 – 70 μm for these purposes.

The fiber has high buoyancy and water repellency, well moistened by hydrocarbons, and production of them from waste provides a lower cost compared to fiber derived by traditional methods.

It is shown that fibers from polypropylene can be used in filtration processes for purification of oily wastewater. Polypropylene fiber has a greater sorption capacity and a higher degree of water purification in comparison with sipron fiber which is traditionally used for these purposes.

An additional advantage of polypropylene fiber is reusability in the mode "absorption-regeneration".

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