Melt electrospinning of polyethylene fibres for oil collection from water surface

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Abstract. Polyethylene nonwoven materials were obtained by the melt electrospinning. The average fiber diameter in the produced nonwovens was 5.3 μm, and the packing density was estimated as 5.2%. Wide-angle X-ray diffraction analysis showed that the polymer does not undergo significant changes in the supramolecular structure during electrospinning process: both pellets and fibers are characterized by the presence of reflections typical for the orthorhombic crystal lattice of polyethylene. The obtained materials demonstrate high hydrophobicity and oleophilicity, which allows using them as sorbents for oil spills removal. The maximum motor oil sorption capacity of the resulting nonwovens was 96 g/g.

1. Introduction
One of the key requirements to any modern technology is its environmental safety. Nevertheless, it is impossible to completely avoid the risks of catastrophic accidents. Accidents in oil and petrochemical industries lead to environmental pollution by liquid hydrocarbons. For example, the Deepwater Horizon drilling rig explosion in 2010 and subsequent fire resulted in its sinking led to a massive spill of about 5 million barrels of oil in the Gulf of Mexico [1, 2]. Therefore, development of sorbent materials for quick and safety oil spills cleanup is of current interest.

The main requirements for those sorbents are their oleophilicity and hydrophobicity, which, on the one hand, allows oil passing for their sorption, and on the other hand, do not pass water through the filter. Moreover, the material should have a high sorption capacity and the ability to subsequently desorb, allowing its regeneration for multiple usages. Finally, the material should be not toxic, easy to produce and cheap [3].

All these requirements are met by nonwoven materials obtained by melt electrospinning of polyolefins (polyethylene, polypropylene, etc.). These materials are characterized by high porosity (more than 90%), which will allow to sorb a large amount of oil in the interfiber space, as well as by a high chemical resistance to most organic media. In addition, due to the absence of organic solvents, as well as the low cost of the original polyolefins, the obtained materials are cheap, and the melt process is more environmentally friendly compared to the “traditional” solution electrospinning method. Nevertheless, studies of melt electrospinning of polyethylene have been limited in the literature to only a few publications [4, 5], in which neither the structure of the fibers nor their wettability or sorption properties are discussed.

Thus, the present study is aimed at fabrication and characterization of morphology, structure and oil sorption properties of nonwoven materials by melt electrospinning of polyethylene.
2. Experimental

2.1. Electrospinning
Fibers were spun from low-density polyethylene 108 (the density of 0.9185 g/cm³, the melt index of 2.2). An experimental setup based on a single screw extruder Brabender Plasti-Corder PLE-330 with four heating zones (Figure 1) was used. To prevent premature degradation of the polymer, the temperature was set at 140°C in the first zone of the extruder and at 200°C in the second and third zones. Electrospinning was performed at 350°C. The extruder was grounded, and the high voltage (135 kV) was applied to the collecting electrode made in the form of a cylindrical drum equipped with an electric motor drive. The diameter and width of the drum were 15 and 25 cm, respectively; the rotation speed was 1.5-2 rpm. The distance between the nozzle and the collector was 45 cm and the volume flow rate of the polymer melt was ~4 mL/h.

![Figure 1. Experimental setup for producing nonwoven materials by melt electrospinning: 1 – high voltage supply (Spellman SL130PN30), 2 – extruder, 3 – screw, 4 – nozzle, 5 – fiber, 6 – collecting device.](image)

2.2. Characterization
Morphology of nonwoven materials was studied using a scanning electron microscope Hitachi TM4000Plus at an accelerating voltage of 5 kV; and fiber diameters were evaluated using ImageJ 1.49 software. IR spectra were recorded with a Thermo Scientific Nicolet iS5 spectrometer with an iD5 ATR accessory. X-ray diffraction analysis of the samples was performed on Rigaku SmartLab diffractometer (CuKα-radiation, $\lambda = 1.5408$ Å, scan rate – 2 deg/min). Contact angles were measured with a KRUSS DSA30E system, the droplet volume was 5 μl.

2.3. Oil sorption/desorption measurements
The maximum sorption capacity of the material was determined using 5W-40 synthetic motor oil (produced by ExxonMobil) as a reference test medium. Scheme of the oil sorption and desorption experiment is shown in the Figure 2. A 4x4 cm nonwoven sample was weighed, placed in a beaker containing 200 ml of motor oil for 5 minutes, and then removed, held for 30 seconds to drain the unsorbed oil and re-weighed. After the initial sorption test, the material was placed into the sand core funnel and oil was removed from the oil-loaded sample with a vacuum pump for 2 minutes and then the sample was weighed again to determine the mass of residual oil. The sorption/desorption process was repeated for five cycles to evaluate the reusability and recoverability of the fibrous material.
3. Results and discussion

3.1. Material characterization

As noted in studies on electrospinning of nonwoven materials from polymer melts, the viscosity and conductivity are key parameters determining the mean fiber diameter. An increase in temperature leads both to a decrease in viscosity and an increase in the electrical conductivity of the melt, which makes it possible to obtain thinner fibers [5-8]. As a result, the materials obtained at the nozzle temperature of 350°C consist of fibers with a diameter of 1.5 to 12 μm (the average diameter is 5.3 μm). The fibers have smooth surface and round shape (Figure 3a). The whole nonwoven fabric sample has a size of 20x43 cm, a surface density of 32 g/m² and a packing density of 5.2% (i.e., the porosity is 94.8%). Moreover, based on the melt flow rate and the average fiber diameter, the linear speed of fiber formation can be estimated at 40–60 m/s.

It should be noted that the process of melt electrospinning of polyethylene begins only at a temperature of about 290°C. In comparison, fibers from polyamide-6 with similar viscosity can be produced at 250°C [7]. Thus, the melt conductivity is the factor determining the beginning of the electrospinning process, which is 4-5 orders of magnitude lower in polyethylene than polyamide-6.

It should be noted that the obtained nonwoven materials demonstrate significant hydrophobicity and oleophilicity (Figure 3b). The static water contact angle exceeds 140 degrees, and a drop of oil is instantly absorbed into the surface, which allows using these nonwovens to remove oil spills from water surface.

3.2. Structural properties

The process of melt electrospinning occurs with an extremely high drawing rate of fibers and their rapid solidification in the electric field; as a consequence, specific supramolecular structures may appear in the polymer. For example, during melt electrospinning a transition from stable α-form crystals to
metastable $\gamma$-form in polyamide-6 and from stable $\alpha$-form to mesophase in polypropylene were reported [7, 8]. However, wide-angle X-ray diffraction analysis reveals no such significant changes in polyethylene. Reflections typical for the orthorhombic crystal lattice of polyethylene [9, 10] are observed in both the polymer pellets and nonwoven materials: (110) at 21.5°, (200) at 23.9°, (210) at 30.1° and (020) at 36.4° (Figure 4a).

In the FTIR spectra of the samples, characteristic bands of polyolefins [11] are observed, i.e. antisymmetric and symmetric C-H stretching in methylene groups at 2919 and 2848 cm$^{-1}$; C–H bending vibrations in methylene groups: scissoring at 1472 and 1464 cm$^{-1}$ and rocking at 718 and 729 cm$^{-1}$ (Figure 4b). Adsorption band at 1376 cm$^{-1}$ can be assigned to C–H bending vibrations in methyl groups (ramifications and terminal groups). In the nonwoven material, a new absorption bands are observed: a broad band at 1750-1700 cm$^{-1}$ and a very weak band at 1167 cm$^{-1}$. These absorption bands can be attributed to the stretching vibrations of the C=O and C–O groups arising from the thermal oxidation of polyethylene during electrospinning [12].

![Figure 4. XRD patterns (a) and FTIR spectra (b) of the PE samples: 1 – pellet, 2 – nonwoven material.](image)

3.3. Oil sorption capacity and reusability of materials
One of the applications of nonwoven materials is the removal of oil spills from the surface of the water, and the sorption capacity of commercially available materials usually does not exceed 30 g/g [13]. The nonwoven materials obtained in this work are characterized by significantly higher maximum sorption capacity of 96 g/g for motor oil. In addition, the reusability of the material was investigated; and the sorption capacities of nonwovens at different sorption-desorption cycles are illustrated in Figure 5.

![Figure 5. Oil retained in sample versus the sorption/desorption cycles.](image)
the material during vacuum oil desorption. The residual mass of oil in all desorption cycles is in the range of 3-4 g/g.

4. Conclusion

Thus, in this work nonwoven materials with an average fiber diameter of 5.3 μm and porosity of 94.8% were obtained by electrospinning of polyethylene melt. WAXD studies showed that the supramolecular structure of the polymer does not undergo significant changes in the process of electrospinning. The produced fibers demonstrate significant hydrophobicity (contact angle exceeds 140 degrees) and oil absorption, and their maximum sorption capacity for motor oil is 96 g/g.

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