

Structure and properties of highly porous polymer materials obtained by polymerization of an external phase of highly concentrated emulsions

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Abstract

Relevance of the research topic

Porous polymer materials are being actively studied as materials for cell engineering, catalysis, membrane technologies, and sorption of petroleum products, antibiotics and heavy metals. Such materials can be obtained by various methods, including polymerization of an external phase of water-in-oil highly concentrated emulsions. Such emulsions are also called high internal phase emulsions (HIPE). Using this method, it is possible to set the properties of highly porous polymer materials even at the stage of obtaining the pristine HIPE by varying the proportion of the dispersed phase and composition: the type and concentration of the surfactant, the concentration of the electrolyte in the internal phase, etc. However, due to the occurrence of coalescence and Ostwald ripening in the stock HIPE, the structure of the pores in the polymer material can change, and their size can be much larger than the droplet size of the internal phase.

A necessary condition for the structure of the porous polymer material to be as close as possible to the structure of the HIPE is to ensure the high stability of the pristine emulsion. It should be noted that the conditions for the formation of traditional HIPE with non-polar hydrocarbons in an external phase have been fairly well studied at the present time. HIPE with monomers in an external phase have been studied to a much lesser extent. Moreover, many monomers have surface-active properties, which can affect the stability of HIPE. In addition, such polymeric materials are often prepared by thermally initiated radical polymerization. At elevated temperatures, an increase in the rate of coalescence and Ostwald ripening can occur and, as a consequence, a change in the structure of a highly porous polymer.

If comonomers such as styrene and divinylbenzene, which are widespread in the polymer industry, are used as an external phase of emulsions, an inexpensive but effective sorbent can be obtained for removing oil products from the surface of water. To improve the sorption properties of the sorbent and the possibility of its extraction using a magnetic field after the end of sorption, it is also advisable to use composite materials based on a porous polymer matrix and magnetic nanoparticles as filler.

Thus, an urgent task is to study the stability of HIPE containing monomers in an external phase and to create on their basis polymer materials with high porosity and controlled pore size.

Purpose and main objectives of the study

To establish the effect of the stability of HIPE containing styrene and divinylbenzene in a dispersion medium on the structure and properties of highly porous polymeric materials obtained on the basis of such emulsions for removing oil products from the water surface.

To achieve this goal, the following tasks were set:

1. Establish the dependence of the aggregate stability of HIPE with a dispersion medium of styrene and divinylbenzene on their composition and production conditions;
2. Show the effect of stability of HIPE on the structure and properties of porous polymeric materials obtained on their basis;
3. To determine the effect of the structure and size of pores in highly porous copolymers of styrene and divinylbenzene on the sorption properties and selectivity of absorption of oil products in relation to water;

4. To prepare composite highly porous polymer materials with magnetite nanoparticles as fillers to improve the sorption properties of porous styrene and divinylbenzene copolymers in relation to oil products and water;

5. Show the absence of toxic properties of the prepared highly porous copolymers of styrene and divinylbenzene when removing oil products from the water surface.

Scientific novelty

A relationship has been established between the structure, pore size in porous materials made of polystyrene and styrene-divinylbenzene copolymer, and the resistance of the stock HIPE to coalescence and Ostwald ripening.

It was shown that HIPE with monomers in an external phase with an internal phase fraction of 0.95 were resistant to coalescence and sedimentation at 25 and 65 °C at a sorbitan oleate concentration of 10-20 vol.%. With the inclusion of HIPE divinylbenzene in the composition of the external phase, the stability of emulsions to coalescence decreased, most dramatically at sorbitan oleate concentrations <10 vol.%. And, to a lesser extent, at a sorbitan oleate concentration of 10–20 vol.%.

When an indifferent electrolyte, for example, NaCl, was included in the composition of the water internal phase of HIPE, the rate of Ostwald ripening and coalescence at temperatures of 25 and 65 °C decreased and at a NaCl concentration of 0.1 wt.% it decreased to almost zero values at 25 °C. It has been shown that when polymerization is initiated with oil-soluble benzoyl peroxide, porous polymeric materials with smaller pores are obtained in the presence of an indifferent electrolyte (for example, NaCl) in the internal phase at a concentration of ≥ 0.02 wt%.

It was found that the formation and size of secondary holes in the pore walls of highly porous styrene-divinylbenzene copolymers was influenced by the amount of surfactant or indifferent electrolyte in the HIPE. With an increase in the concentration of Span 80 in the HIPE or NaCl in the dispersed phase of the HIPE, the diameter of the secondary holes decreased linearly with a decrease in the average pore size. It has been shown that it is possible to obtain porous copolymers of styrene and divinylbenzene with the same average pore diameter and different average secondary throats diameters.

It was shown that with an increase in the concentration of Fe₃O₄ nanoparticles, the pore size of materials from a copolymer of styrene and divinylbenzene decreased, the rate of sorption of oil products increased, and the rate of water sorption decreased, presumably due to an increase in the hydrophobicity of the pore surface with an increase in their roughness and a decrease in the amount of surfactant on the interface.

Theoretical and practical significance

A method has been developed and conditions have been determined for obtaining highly porous materials from styrene and divinylbenzene copolymers with a controlled pore size in the range of 3-45 microns during the polymerization of an external phase of HIPE.

It was found that there is a critical pore size at which the rate of sorption of oil in the initial period of time is equal to the rate of sorption of water, in pores of a smaller size, the rate of sorption of oil is higher than the rate of sorption of water, and of a larger size, lower. The presence of a critical pore size makes it possible to develop porous polymeric materials for the selective sorption of petroleum products.

Samples of highly porous styrene and divinylbenzene copolymers with a porosity of up to 95% for the sorption of petroleum products with a viscosity of 1 to 670 mPa·s with a capacity of up to 25 kg/kg have been obtained. In this case, the capacity of sorbents for water, both

bidistilled water and model seawater, did not exceed 3 kg/kg. The samples remained buoyant for more than 7 days.

It is shown that due to the high hydrophobicity of the surface of the developed sorbents, the water absorbed by them was displaced by oil products over time, which increases their selectivity when removing thin films of oil products from the surface of water bodies.

An analysis of the magnitude of the coercive force and the shape of the hysteresis loops of highly porous styrene and divinylbenzene copolymers with Fe_3O_4 nanoparticles showed that these sorbents were weak magnetically hard materials. However, their hysteresis properties indicate the possibility of collecting those using magnets when using petroleum products as sorbents.

The absence of acute toxic effects on daphnia *Daphnia magna* and the cells of *Scenedesmus quadricauda* algae was shown in accordance with the methods FR 1.39.2001.00283 and FR 1.39.2007.03223.

Provisions for Defense

1. Influence of the concentration of sorbitan monooleate, the ratio of styrene and divinylbenzene in the external phase, the concentration of NaCl in the internal phase of HIPE, and magnetite nanoparticles 10 and 40 nm in size on the dispersity and stability of emulsions with a fraction of the internal phase from 0.75 to 0.95.
2. Influence of the concentration of sorbitan monooleate, the ratio of styrene and divinylbenzene in the external phase of HIPE, the concentration of NaCl in the internal phase of emulsions, the concentration of polymerization initiators of benzyl peroxide and ammonium persulfate, magnetite nanoparticles on the pore size and secondary throats in porous styrene and divinylbenzene copolymers obtained by polymerization of an external phase of HIPE.
3. Influence of the pore size in porous copolymers of styrene and divinylbenzene on their sorption properties when absorbing oil products with different viscosity and water.