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A novel alternative to free oil remediation and recovery: Foamy absorbents designed from low molecular paraffinic waste

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ABSTRACT

This study focuses on preparing porous, hydrophobic, and oleophilic hydrocarbon-based foams applicable for removing free oils from water surfaces. Paraffinic waste material generated during industrial production of low-density polyethylene (Qatar Petrochemical Company) was used for the preparation of foamy, elastic structures through crosslinking of short aliphatic chains by dicumyl peroxide and foaming by 1,1'-azobiscarbamide. The porosity of the foam determined by computer microtomography was 58.9%, and the bulk density was 0.42 g. cm⁻³. The sorption ability of the foam was tested using diesel oil, motor oil, and heavy crude oil. The absorption capacity of foam was characterized as the ratio between the mass of oil absorbed by the foam and the mass of a neat foam (S_w) and as the ratio between the volume of oil absorbed by the foam and the volume of a neat foam (S_v). The absorption capacities of the new foam reported in this study (referred to here as Qwax foam) are 6.6 ± 0.3 g/g, or 3.3 ± 0.2 cm³/cm³ for diesel oil, 3.9 ± 0.4 g/g or 1.9 ± 0.3 cm³/cm³ for motor oil, and 3.4 ± 0.2 g/g or 1.4 ± 0.4 cm³/cm³ for crude oil. To compare the sorption ability of Qwax foam with some standard foams, the absorption capacities of highly porous commercial polyurethane (*PU*) and melamine (*MA*) foams were investigated under the same conditions. These foams showed much higher sorption capacity considering the S_w parameter as a reference; however, there was a lower sorption capacity compared to parameter S_v . In the last paragraph, the suitability and the relevancy of parameters S_w and S_v for a comparison of the absorption capacity of foams were theoretically analyzed.

Keywords: Oil removal, foams, absorption capacity, porosity

1. Introduction

Large-scale oil spills accidents, as well as a large amount of oily polluted wastewater coming from the petrochemical industry [1-4], metal processing, the food industry, and households [5,6], have a serious impact on the biosphere, aquatic life, and, from a practical point of view, on the enhanced costs associated with water cleaning for common uses [1]. The morphology of water/oil systems primarily

determines the treatment strategy. Oil spills mainly occur in the form of free oil; however, if the time factor is taken into account, a free oil can also be formed as a final stage of intrinsic or induced de-emulsification processes in oil in water (o/w) emulsions and mixtures due to their limited kinetic stability. This stability is perturbed over time, leading to free oil formation through different mechanisms, such as coalescence, coagulation, and creaming [7]. Various routes and technologies have been developed and used practically for free oil, including mechanical, chemical, thermal, and biological methods [8,9]. The utilization of sorbent materials is a suitable approach for the removal of free oil from water surfaces, mainly if the oil layer is thin and spread over a large area, where mechanical removal cannot be effectively applied. Powdered sorbent media involve inorganic porous materials (ash, talc, clay, silica aerogel, etc.) [10,11], and organic natural materials (agricultural waste, cotton mats, wood), which are mostly cheap and readily available, but they possess a low sorption ability and limited possibility for oil removal (recovery), which contributes to the accumulation of solid waste [12,13]. For this reason, new sorbent media have been developed over the last decades, and polymeric sorbents belong to the most promising media due to their high sorption ability, easy synthesis and tuning of surface properties, the possibility of oil recovery, and relatively low price [14]. Oil can be captured by sorbents on their surface, mostly having high surface porosity, increasing a specific surface area (adsorption), and in their bulk structure (absorption) [14]. The bulk structure is composed of a material itself (matrix) and internal pores formed by air (foams, sponges). Materials that absorb oil (or any other liquid) in their bulk can swell if a liquid is mostly localized within a solid matrix, or they may rest in their original shape and volume if the liquid occupies only empty space (pores) within a structure. Nonswellable, highly porous foams (e.g., polyurethane (*PU*) and melamine (*MA*)) are the most common polymer structures employed for free oil removal. *PU* and *MA* foams attract particular interest due to their very high porosity (95-99 vol%), mechanical (compression, bending), and thermal stability, worldwide availability (common *PU* and *MA* foams used for cleaning are easily available, simple use and low price [15,16]. *MA* and *PU* foams are thermosetting materials that do not swell when absorbing liquids due to their highly crosslinked structure [17,18]. These foams can also be easily chemically and physically modified to tune their wettability [19]. *MA* and *PU* foams strongly absorb both oils and water, which is not favorable for practical use, so suppression of water sorption through hydrophobic treatment on the surface or in bulk is an essential requirement [18,29].

Among other common polymeric sorbents are polymeric fibers (e.g., polypropylene, polystyrene) [20,21] and polydimethylsiloxane [22,23]. Melt-blown polypropylene (*PP*) pads and booms [24,25] are the most commonly used polymeric oil sorbent materials, adsorbing oil within their interstices via capillary forces.

Another group of polymeric materials is crosslinked elastomers (e.g., styrene-butadienestyrene copolymer, butyl rubber) [26,27] and thermoplastics, which are inherently hydrophobic, unlike *MA* and *PU*, and thus they need not be (but can be) additionally hydrophobised. These materials, dependent on their composition, porosity, and degree of crosslinking, can absorb a significant amount of oil undergoing swelling of their structure. Very interesting are specially designed polyolefin-based absorbents synthesized by olefin polymerization from suitable vinyl monomers with high porosity, an ability to swell, as well as natural hydrophobicity and oleophilicity [28-32]. Nam et al. recently published a set of papers related to the synthesis, characterization, and large-scale application of such polymer network sorbents (called i-Petrogel) [28-32]. Two grades of polyolefin-based materials were investigated, namely, semicrystalline poly(ethylene-co-1-octene), which is commonly known as linear low-density polyethylene (*LLDPE*), with the low- and crosslinked amorphous copolymer poly(1-decene-co-divinylbenzene), marked as x-d-DVB [28-32].

The study presented in this paper is focused on the preparation of porous, hydrophobic, and hydrophilic hydrocarbon-based foams from paraffinic waste material generated during the industrial production of low-density polyethylene. The absorption capacity of the foams was compared with the absorption capacity of commercial PU and MA foams. Analysis of the suitability of some absorption characteristics was also performed.

2. Materials and methods

2.1. Materials

Waste paraffin wax (Q_{wax}) was obtained from Qatar Petrochemical Company, QAPCO (*Qatar*). It is a sticky, highly viscous waste product of the polymerization process of low-density polyethylene (*LDPE*). It is a mixture of various alkanes with a number of carbons in the range from C33 to C128. The specific density is 0.88 g/cm^3 , the melting point is $102 \text{ }^\circ\text{C}$, and the specific enthalpy of melting enthalpy is 20 J/g . The very low enthalpy of melting indicates a very low degree of crystallinity due to the highly branched chains representing obstacles to the regular folding of chains.

A crosslinking of Q_{wax} was performed by dicumyl peroxide (*DCP*) (SIGMA ALDRICH, USA). Foaming was performed using the blowing agent Genitron (Genitron AC2, Schering Polymer Additives, England), which is the masterbatch consisting of 40 wt% 1,1'-azobiscarbamide within LDPE. Diesel oil (the specific density = 0.850 g.cm^{-3} , the dynamic viscosity = 3.4 mPa.s), motor oil (the specific density = 0.873 g.cm^{-3} , the dynamic viscosity = 493 mPa.s), and heavy crude oil (the specific density = 0.990 g.cm^{-3} , the dynamic viscosity = 12 mPa.s) were used for absorption experiments. The specific density and the dynamic viscosity of the used oils were determined at $20 \text{ }^\circ\text{C}$.

2.2. Foam preparation

Q_{wax} was melted at $140 \text{ }^\circ\text{C}$ in a beaker using a magnetic stirrer, and then the blowing agent Genitron (10 phr) and DCP (10 phr) were added. The mixture was stirred for 10 min until a homogeneous compound was obtained. The liquid mixture was poured into the cylinder-shaped mold, inserted into a mounting press, and heated at $180 \text{ }^\circ\text{C}$ for 10 min. During this time, DCP and Genitron decomposed, leading to crosslinking of the material and the formation of gaseous products within the bulk material. Then, the form was removed from the press, which led to the expansion of gasses and foaming of material. Finally, the foams were put into a vacuum oven at $80 \text{ }^\circ\text{C}$ for six hours to release residual gaseous products from the material. The preparation route is shown in **Fig. 1**.

2.3. Absorption test

Absorption tests were performed using cuboid-shaped samples with dimensions of $2 \times 1 \times 1 \text{ cm}$. The samples were immersed in oil at $22 \text{ }^\circ\text{C}$, and the mass of the samples was measured after selected periods. Each experiment was repeated three times. These data were used to evaluate the kinetics of absorption. The reuse of foams was tested by multiple sorption/desorption experiments. For this purpose, the foams were immersed in the oils for six hours, then the oil was squeezed out, and the foam was immersed into the oil again, without any additional cleaning or treatment. This procedure was repeated four times. The removal of oil from saturated samples was realized by squeezing in a syringe, as shown in **Fig. 2**. The syringe was used to ensure the same deformation of all samples.

The porosity of the sample was investigated at a cut disk 5 mm in diameter and 10 mm in height using computer microtomography (*CT*) on a SkyScan Unit (Model 1174, Bruker, New York, NY, USA). The device was equipped with an *X – ray* power source (20-50 kV and maximum power 40 W) and *X – ray* detector (Bruker, New York, NY, USA). The CCD 1.3 Mpix unit was coupled to a scintillator by a lens with a 1:6 zoom range. Projection images were taken at angular increments of 0.3 ° at a tube voltage of 31 kV and a current of 529 μ A. The duration of exposure was set to 10 s without the use of a filter. 3D reconstructions were created via preinstalled *CT* image analysis software e v1.16.4.1, Bruker, New York, NY, USA).

2.4. SEM analysis

The morphology of foams was characterized by a Nova Nano SEM 450 scanning electron microscope (SEM, Osaka, Japan) operating at 20 kV. Cross-section of foams was done by a sharp blade.

2.5. DMA analysis

A dynamic mechanical analyzer (*DMA 1*, Mettler Toledo, Switzerland) was used to characterize the dynamic mechanical properties at various temperatures in compression mode. The measurements were performed at 1 Hz in the linear viscoelastic region, and the deformation was set to 3% for a broad temperature range and 10% for measurements from 0 °C to 70 °C. The temperature sweeps from –150 to 40 °C and from 0 °C to 70 °C were measured, and the storage modulus and tan delta were evaluated as crucial parameters.



Fig. 1. a.) Mixing of components, b.) casting into the form, c.) crosslinking/foaming, d.) cleaning in an oven, e.) Qwax foam.

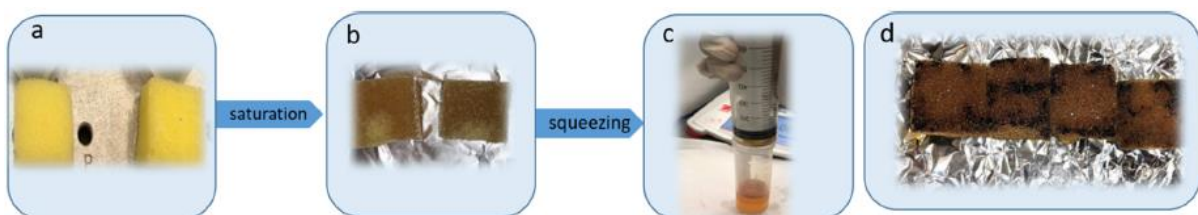


Fig. 2. Squeezing of oil from a foam. a.) a foam before immersion in crude oil, b.) a foam after immersion in oil, c.) oil removal from a foam by squeezing, d.) a foam after squeezing.

2.6. Thermogravimetry (TGA)

The thermal stability of neat *Qwax* and *Qwax* foam was characterized using a TGA 4000 (Perkin Elmer, Greenville, SC, USA) in the temperature range from 30 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.7. Wettability measurement

The OCA35 optical system (Data Physics, Filderstadt, Germany) was employed for the characterization of the surface wettability of the samples by the sessile drop technique. Distilled water and crude oil were used as testing liquids. The experiments were carried out in both air and underwater (for crude oil). A volume of 1 μ L of each testing liquid was used. The average values were calculated from ten measurements.

2.8. Surface topography analysis

The Leica DCM8 profilometer (Leica microsystems, Wetzlar, Germany) was used to analyze surface topography. Images were recorded using a 20 x objective lens from 876.55 x 659.83 μ m² surface area. The surface roughness was evaluated by the mean of arithmetic height (*S_a*) over the entire analyzed area.

3. Results and discussion

3.1. Characterization of crosslinking efficiency and thermal stability

Crosslinking plays an important role in the stability of the final foamy structure. It suppresses the collapse of pores during foaming and ensures an appropriate mechanical strength of the final product. The foams presented in this work are prepared from low molecular weight waxes where crosslinking is vital for their transformation from a soft, waxy state into solid materials with sufficient mechanical properties, enabling a simple manipulation and multiple squeezing.

Prior to foaming, the efficiency of crosslinking was tested using various concentrations of DCP. The efficiency of crosslinking was characterized in terms of insoluble (*gel*) content. The gel content (*g*) was determined gravimetrically after 24 h of extraction of the samples in boiling xylene and calculated from Eq.(1). Three samples were used for gel content determination. Xylene was changed every eight hours. The dependence of the gel content on the DCP concentration is shown in **Fig. 3**.

$$g = \frac{m_{extr}}{m_0} \times 100\% \quad (1)$$

where m_{extr} [g] is the mass of the sample after extraction, and m_0 [g] is the initial mass of the sample.

The *DCP* concentration must be higher than 9 phr to obtain sufficient crosslinking efficiency. It is clear that the *DCP* content is relatively high, especially compared with the crosslinking of standard grades of polyethylene. Polyolefines, unlike oligomers and paraffin waxes, have a very high molar mass (e.g., the molar mass of high-density polyethylene is in the range from 500,000 to 1,000,000 g/mol); therefore, a very low concentration of peroxide (0.5-2 wt%) is needed to ensure almost complete crosslinking characterized by a gel content over 99% [33-37].

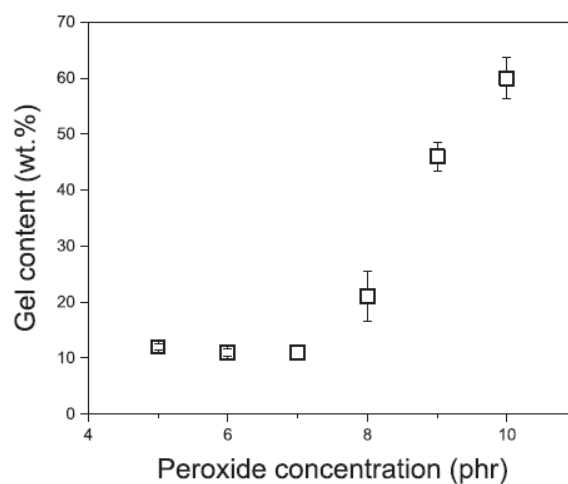


Fig. 3. Gel content of crosslinked Qwax as a function of peroxide concentration.

The crosslinking of oligomers and paraffin requires a much higher peroxide content due to the low molar mass, resulting in a lower content of reaction sites [38,39]. A *DCP* content of 10 phr was selected for further experiments, and various portions of the foaming agent (Geni-tron) were tested. The *Qwax* foam used for further tests was prepared using 10 phr of *DSC* and 5 phr of Genitron, and its bulk density was 0.42 g.cm^{-3} , and porosity was 58.9 vol%.

The thermal stability of both neat *Qwax* and foam was tested by *TGA*, and degradation curves are shown in **Fig. 4**. Both degradation curves are almost identical, indicating that crosslinking does not influence the thermal stability of foams. Both materials are stable up to 360 °C without any weight loss. *TGA* also showed some residues within foam structures originating from the decomposition of both *DCP* and Geni-tron, which did not release foam during preparation. However, all these residues released the material after drying in the oven.

Differential scanning calorimetry showed compression of the crystalline phase, indicating that the skeleton forming the foam is almost entirely amorphous. A decrease or even a suppression of the crystalline phase is indicated with a decrease or disappearance of a peak for the melting point in the *DSC* curve. Crosslinks play the role of defect centers, which suppress the folding of (macro)molecular chains and thus decrease the sizes of the lamellar crystals. Even a small number of crosslinks significantly reduce the crystallinity of *LLDPE* [40,41].

3.2. Foam structure analysis

SEM images show a relatively uniform pore distribution across the *Qwax* foam sample, as seen in **Fig. 5**. The pores had a spherical/oval shape, and the average pore size was calculated through ImageJ software and found to be approximately 500 μm . The main disadvantage of this technique is the very small representative area that is presented, the pore content cannot be determined, and the characterization of morphology by *CT* (**Fig. 6**) is more accurate. This is a noncontact method that avoids deformation of the pores after cutting/breaking, as usually occurs in the case of samples for *SEM* investigation. The pore content determined by *CT* was found to be 58.9 vol%. Results from the 3D image analysis are summarized in **Table 1**.

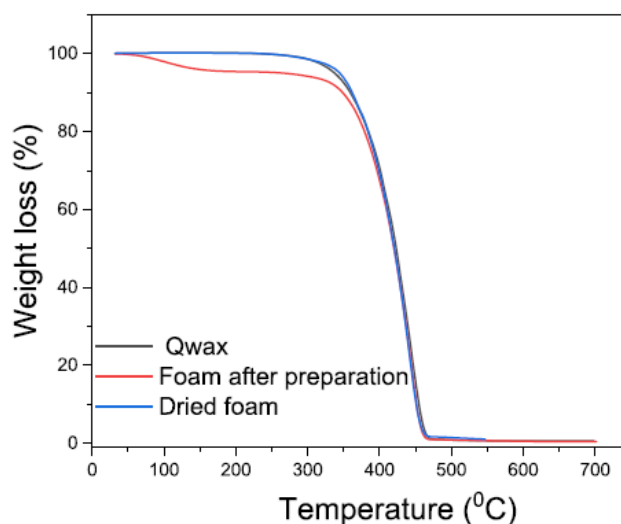


Fig. 4. TGA curves of *Qwax* and *Qwax* foam.

3.3. Surface wettability

Oil and water absorption are crucial in the separation process because, in the presence of both components that are in contact with the sorbent, only one component should rapidly diffuse into the sorbent. One of the important properties of an oil-water separation system is the surface wettability by water and oil [42,43], which is mostly characterized by contact angle measurements for various polar and apolar liquids. The contact angle is strongly dependent not only on the inherent chemical composition of the surface but also on the surface roughness and overall morphology of the specimen surface [42-44]. Indeed, the contact angle for various liquids is.

Different if measured in air and under the liquid. The *Qwax* foam was tested through the measurement of contact angles of oil and water in the air, the contact angle of oils underwater, and the contact angle of water under oils. The measurements of contact angles are shown in Fig. 7A, and the surface topography of *Qwax wax* is shown in Fig. 7B as it is closely related to wettability. The hydrophobic character of foam was observed under both air and oils, as the contact angle values of water are $114 \pm 4^\circ$ and $128 \pm 5^\circ$, respectively. On the other hand, high oleophilicity was observed for *Qwax* foam under both air and water as the contact angle values were 0° (or, more accurately, they were not measurable due to the fast sucking of oils into the tested sample), which is a consequence of the inherent, nonpolar character of paraffin compounds and surface roughness ($Sa = 145.5 \mu\text{m}$). The surface wettability of foam by water and all tested oils is, therefore, very suitable for oil/ water separation. All the oils rapidly sorbed into the foam, whereas water sorption was negligible (less than 0.5 wt% after 24 h of immersion in distilled water), which is a crucial point for the removal of free oil from the water surface.

3.4. Dynamic mechanical analysis (DMA)

The mechanical performance of the *Qwax* foam was characterized by DMA in a temperature region from -160°C to 40°C . The temperature dependences of the storage (G') and loss (G'') moduli, as well as the loss factor (tan delta), are shown in Fig. 8. The storage modulus, characterizing the elastic behavior of the material, varies from approximately 150 MPa to 80 MPa in the glassy region and then

steeply decreases in the elastic (rubber-like) region to approximately 1 MPa at 40 °C. This behavior is similar to that of polyethylene foams [45]. The glass transition temperature T_g of the material was found to be -30.3 °C (Fig. 8b), and the tan delta reached 0.18, showing good damping properties.

For comparison, a DMA measurement was also performed on commercial MA foam, and the G' and G'' parameters are shown in Fig. 9. In this case, glassy and rubbery regions are not distinguished due to the thermosetting character of the MA foam. The rigidity of the foam can be characterized by the storage modulus. G' is only slightly dependent on temperature and ranges from 0.07 MPa at -150 °C to 0.004 MPa at 150 °C.

3.5. Kinetics of absorption

The dependences of the absorption capacity of *Qwax* foam (S_w) on the sorption time are shown in Fig. 10a. The experimental data are compared with selected models, as discussed below.

The mass of absorbed oils was determined in selected intervals up to 360 min of foam immersion into oils. Fig. 10 shows that the sorption is the fastest at short times in all cases, up to approximately 10-15 min after immersion, and then the penetration of oils into foam is significantly slowed. The fastest sorption rate was observed for diesel oil, followed by crude oil and motor oil, which is in line with the increasing dynamic viscosities of the liquids. The rate of sorption (v_s) can be easily quantified from the initial slope (tangent) of the experimental curves. The values of v_s are 0.97, 0.93, and 0.51 [g/g.min⁻¹] for diesel, crude and motor oils, respectively. The mass of the maximum absorbed liquid per the mass of sorbent was determined arbitrarily after six hours of sorption. The following values were found: 6.6, 3.9, and 3.4 g/g for diesel, motor, and crude oil, respectively. The absorption was accomplished with volumetric changes of samples due to swelling. The initial volumes of testing foams increased by 138%, 30%, and 68% for diesel, motor, and crude oil, respectively. Samples were also kept immersed in oils for 24 h, and a small increase in absorbed oil was observed; however, these data were not involved in the modeling of kinetic dependences discussed below to preclude extending the time scale too much.

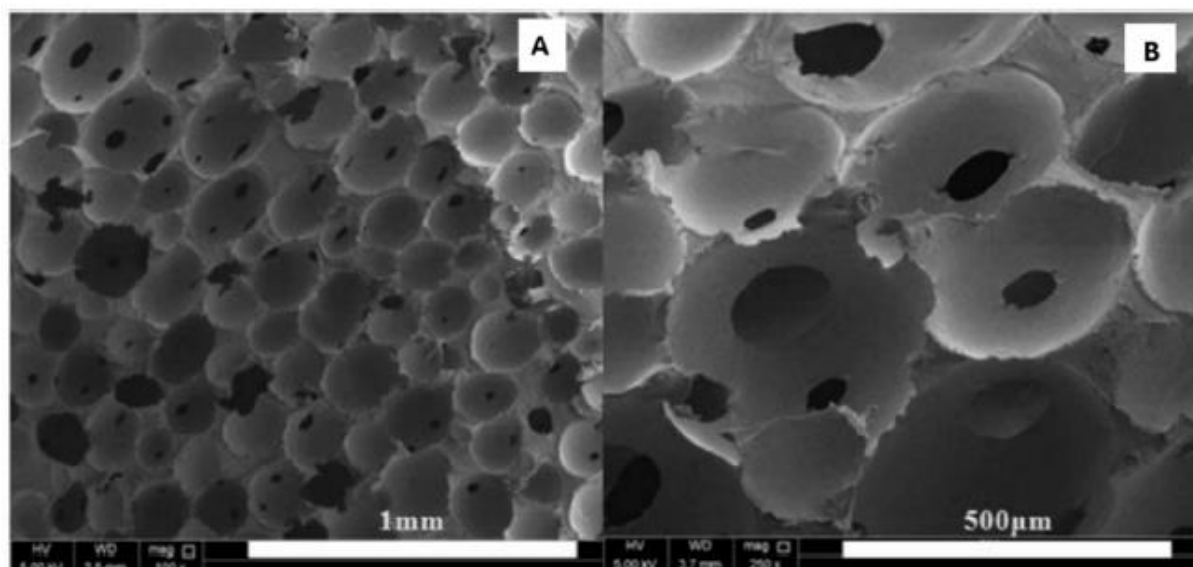


Fig. 5. SEM micrographs: (A) magnification 100x, (B) magnification 250x.

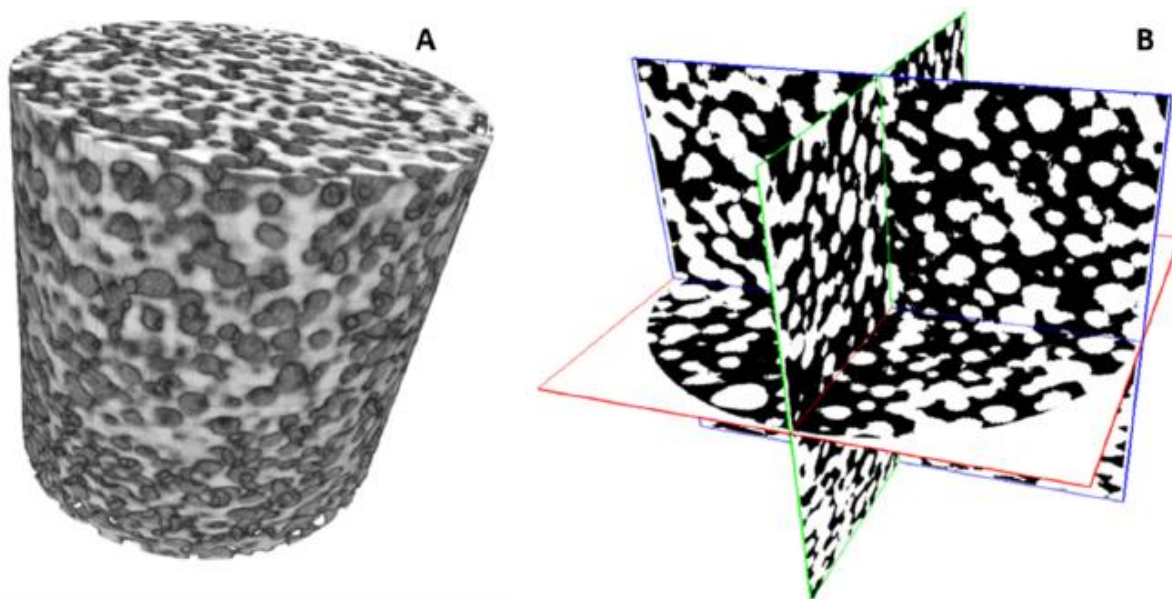


Fig. 6. 3D model of the foam sample (A) and space cross sections (B). The sizes of the samples were 5.5 mm (diameter) and 6 mm (height).

Table 1 Results from 3D image analysis.

| | |
|--------------------------------|-----------------------|
| Total analyzed volume | 139.9 mm ³ |
| Foam volume in analyzed volume | 57.5 mm ³ |
| Volume of open pores | 82.4 mm ³ |
| Volume of closed pores | 0.001 mm ³ |
| Open porosity (percent) | 58.9% |
| Closed porosity (percent) | 0.002% |

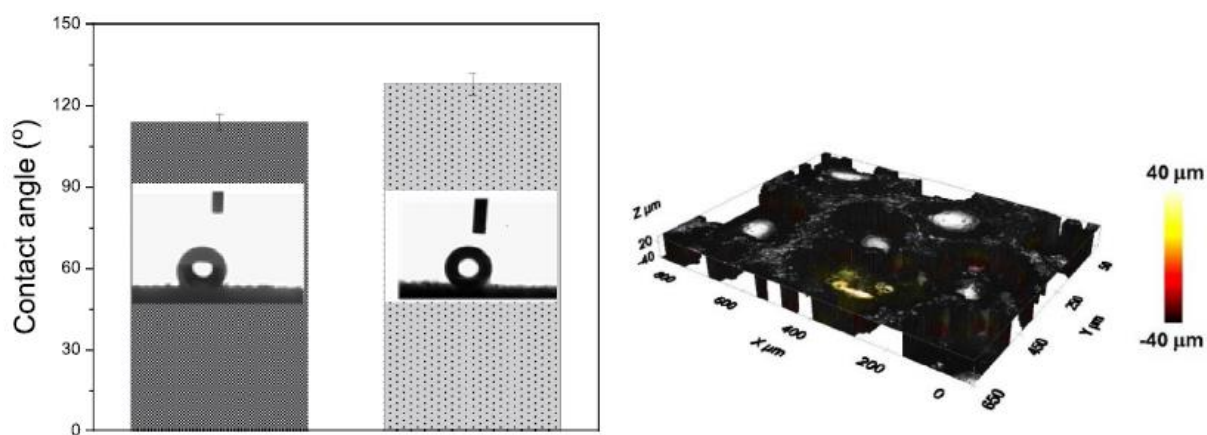


Fig. 7. A) Wettability of foam by water under air, under crude oil, and B) profilometry image.

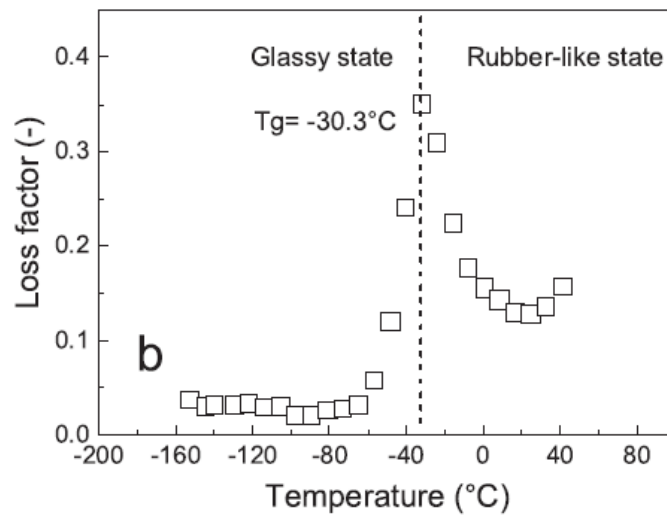
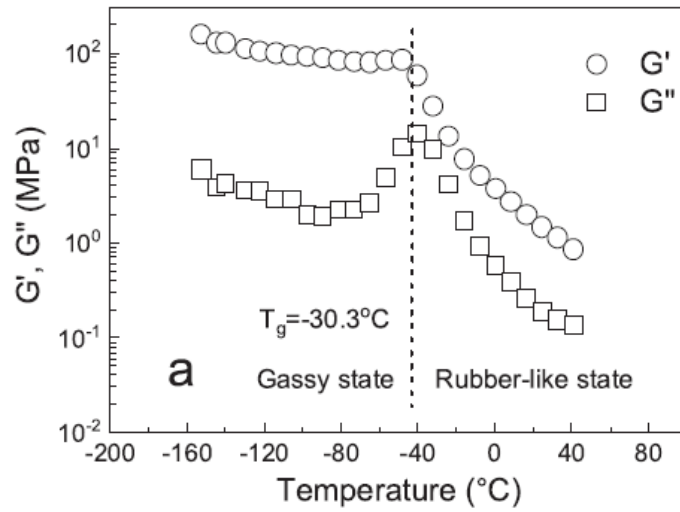


Fig. 8. Temperature dependence of the storage and loss moduli (a) tan delta (b) for the *Qwax* foam crosslinked system.

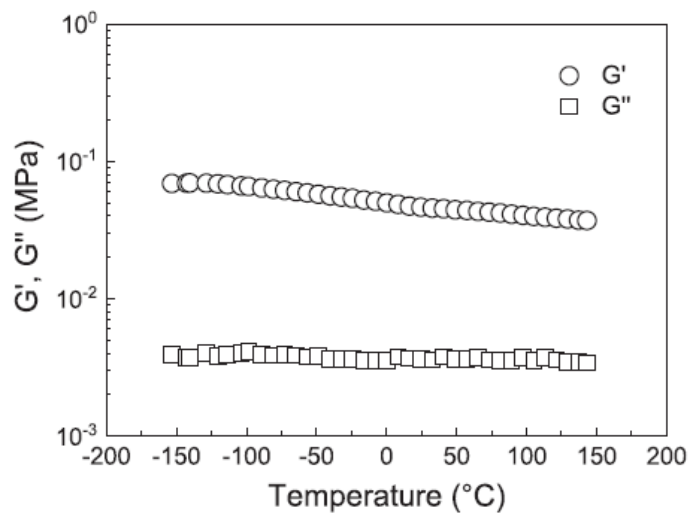


Fig. 9. Temperature dependence of the storage (G') and loss (G'') moduli of *MA* foam.

The time dependence of free oil sorption by porous structures has been frequently studied both experimentally and theoretically [41-44]. This kinetics is frequently described by the same models used for the description of the kinetics of adsorption of low molecular weight species on solid surfaces. The most common models describing the sorption of low molecular weight species from liquids (mostly water) are the pseudo-first-order (*PFOM*) [45], pseudo-second-order (*PSOM*) [46], and Weber-Morris intra-particle diffusion model (*IPD*) [53]. Here, we refer to the original papers only (Table 2).

The Weber-Morris intra-particle diffusion model (*IPD*) is the most frequently applied model for systems in which adsorption is accomplished by diffusion processes. If diffusion is a single rate-limiting process, then all data can be described by a single line; however, it is a rare situation, and many researchers noticed that the adsorption process is governed by more limiting mechanisms, and data cannot be fitted by a single line for the whole time interval. Therefore, the data are divided into more (two-three) segments, and they are fitted separately. This is a significant weakness of this approach [47,48]. More details about the limitations of different kinetic models can be found in Hubbe’s review [49].

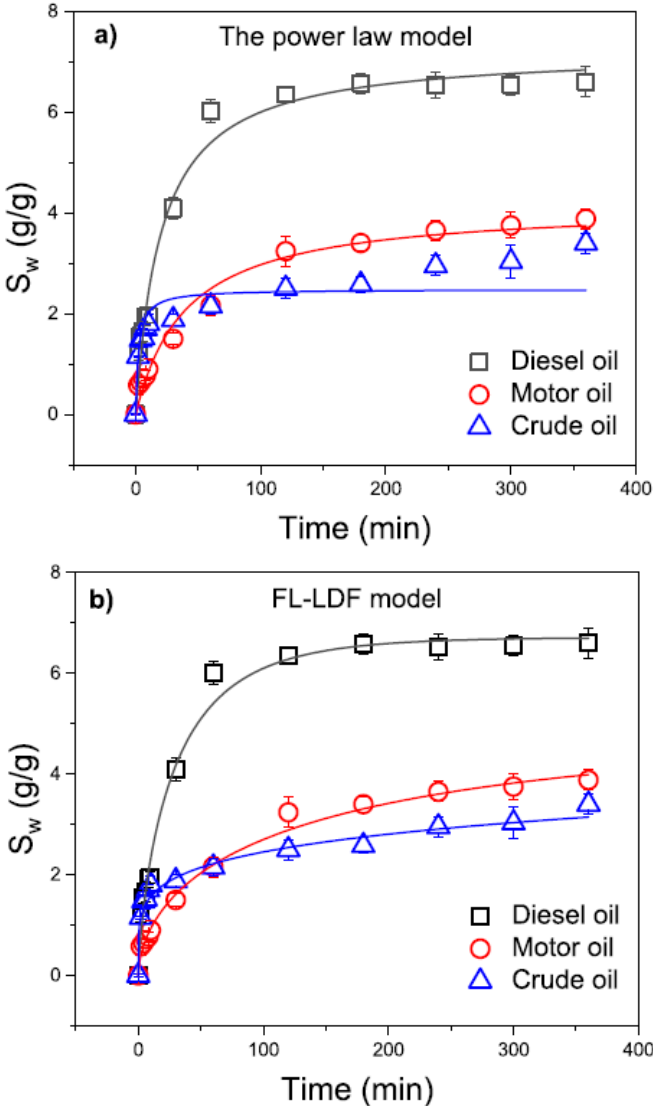


Fig. 10. Absorption capacity (S_w) of *Qwax* foam for diesel, motor, and crude oil compared with the power law model (a) and *FL – LDF* model (b).

The *PFO*, *PSO*, and *IPD* models are frequently used for a description of oil sorption in porous materials and, in some cases, do not always perfectly fit experimental data [41-44]. However, as discussed by Azi-zian [50], it may only be a mathematical coincidence, and fitting parameters may have a questionable physical meaning. The experimental data referred to in this paper are also not describable by those models. The reason is that *PFOM* and *PSOM* have been developed for adsorption and not for absorption, and considerations about monolayer adsorption are included in the preconditions for the derivation of those models.

Table 2 A list of selected kinetic models.

| Model | Parameters | Description |
|--|--|---|
| <u>Pseudo-first-order model</u> [51] $q_t = q_e(1 - e^{-k_1 t})$ | q_e, q_t [g/g] [-amount of adsorbed species per mass of adsorbent in time t , and in equilibrium] k_1 [min^{-1}] is the pseudo-first-order rate constant | <ul style="list-style-type: none"> • monolayer adsorption • more suitable for high initial concentrations • nonlinear fits better describe data |
| <u>Pseudo-second-order model</u> [52] $q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$ | q_e, q_t [g/g] [-the amount of adsorbed species per mass of adsorbent in time t , and in equilibrium] k_1 [min^{-1}] is the pseudo-second-order rate constant | <ul style="list-style-type: none"> • monolayer adsorption • more suitable for low concentrations • nonlinear fits better describe data |
| <u>Intra-particle diffusion model</u> [53] $q_t = k_{ipd} \sqrt{t} + C$ | q_e [g/g] [-the amount of adsorbed species per mass of adsorbent in time t , k_{ipd} [$\text{g/g} \cdot \text{min}^{-1/2}$] is the rate constant for intraparticle diffusion, and C [g/g] is a constant related to the boundary layer thickness | <ul style="list-style-type: none"> • empirical model • adsorption is accomplished by a diffusion process • diffusion is a single rate-limiting process • a diffusion is Fickian |

Additionally, it has been demonstrated that the equilibrium amount of adsorbed species (q_e) is a function of the initial concentration of solute, which is also not relevant for oil absorption. Therefore, for oil absorption studies, instead of the equilibrium adsorbed value, the maximum absorbed value must be defined. Considering these limitations, Azizian et al. [50] developed the so-called ‘fractal-like linear driving force (FL-LDF)’ model (Eq. 2) by sorption of liquids (e.g., oils) by porous materials considering the following physical aspects of the process: (i) “absorption” not “adsorption,” (ii) maximum capacity of adsorbent, (iii) physical meaning of the rate coefficient and (iv) presence of different pores for absorption.

$$m_t = m_{max} [1 - \exp(-D' t^\alpha)] \quad (2)$$

where m_t [g/g] is the mass of absorbed liquid per the mass of sorbent, m_{max} [g/g] is the mass of maximum absorbed liquid per the mass of sorbent, D' [$\text{time}^{-\alpha}$] is the mass transfer coefficient, t [s, min] is time of the experiment duration, and α [–] is dimensionless fractal constant ($0 < \alpha \leq 1$).

To keep the same symbols for the whole text, we introduced the following notation: $m_t \rightarrow S_w(t)$, $m_{max} \rightarrow S_{w,max}$. The comparison of results with the *FL – LDF* model is shown in **Fig. 10**, and the parameters D' ,

and α are summarized in **Table 3**. It is evident that the model fits all the data with high accuracy, confirming its mathematical suitability for a description of experimental results. The meaning of all the parameters is clearly defined; however, their plausibility cannot be verified. We suppose that the validity of this new, interesting model should be confirmed by the determination of parameters D' and α by other, independent methods.

The second model used for the description of experimental data is the generalized non-Fickian diffusional model, initially introduced by Ritger and Peppas [51,52] for the interpretation of a non-Fickian release of drugs from moderately swelling polymeric systems.

$$\frac{M_t}{M_\infty} = kt^n \quad (3)$$

In the original papers, M_t and M_∞ are mass concentrations of a released species at time t , and time approaching infinity, k is a constant involving characteristics of the network (medium) and the species, and n is the diffusional exponent. In general, it is considered that if $n = 1/2$, the model characterizes Fickian diffusion; however, very rigorously, it is essential to point out that parameter n does not necessarily equal $1/2$, even if diffusion is purely Fickian, because this parameter also depends on the geometry of the system. Ritger and Peppas showed that in the case of pure Fickian release of molecules from media of different geometries, the exponent n had limiting values of 0.50, 0.45, and 0.43 for release from slabs, cylinders, and spheres, respectively [51,52]. However, in papers focused on a description of sorption using the power law equation, the influence of sorbent geometry is mostly not taken into account.

Fickian diffusion runs within homogeneous systems without the presence of boundaries, such as pores, swollen and dry regions, and regions with different physical states (glassy, rubber). However, the penetration of oil into the *Qwax* foam is far from Fickian diffusion, as indicated by the values n , which are significantly lower than 0.5. The sorption data of foams for different oils were fitted by Eq. (3), where the term $\frac{M_t}{M_\infty}$ was replaced by the term $S_w(t)$.

The real process involves i.) diffusion of oil into the empty pores filled with air, ii.) diffusion of oil into bulk material (*matrix*), and iii.) the process is accomplished by a volumetric change of the sorbent during sorption. The very high rate of sorption in the first stage (10 min of immersion) is probably caused by the penetration of oil into the pores, which are interconnected due to cracks in the walls. This ensures fast filling of interconnected pores. At the same time, but slower, oil diffuses into the solid *Qwax matrix*. If all available pores are filled, only diffusion into the bulk polymer can proceed.

3.6. Reusability of *Qwax* foam

The multiple uses of sorbents, in general, are a desirable property of all sorbents, regardless of the type of sorbent recovery. Foamy sorbents are frequently recovered by simple mechanical squeezing [13]. In this paper, we included only the results for crude oil sorption, which is the most common pollutant in oil spills. Cycling tests for diesel and motor oil differed only in absolute values, and their involvement is not important in the whole context of this paper. The data recorded in this experiment were the mass of foam after immersion, the mass of foam after squeezing oil out, the mass of squeezed oil, and the dimensions of foam before and after squeezing. The calculated parameters are: i.) the mass of trapped oil/mass neat foam ($m_{trapped}/m_0$), ii.) the mass of released oil/mass of neat foam

($m_{released}/m_0$), iii.) the total mass of absorbed oil/mass neat foam (m_{total}/m_0), iv.) the volume of trapped oil/volume of neat foam ($V_{trapped}/V_0$), v.) the volume of released oil/volume of neat foam ($V_{released}/V_0$), and vi.) the total volume of absorbed oil/volume neat foam (V_{total}/V_0). The parameters characterizing the sorption ability of the foam during four sorption/desorption cycles are summarized in **Table 4**. The volume of the neat foam was 8 cm³ (2 cm x 2 cm x 2 cm). More cycles were not completed because the foam started to lose its mechanical integrity.

Table 4 The parameters characterizing the sorption ability of the foam during four sorption/desorption cycles.

| Sorption parameters | Cycle 1 | Cycle 2 | Cycle 3 | Cycle 4 | Average |
|---------------------|---------|---------|---------|---------|-----------|
| m_{total}/m_0 | 2.05 | 3.53 | 2.95 | 3.44 | 3.1 (0.7) |
| $m_{released}/m_0$ | 1.18 | 1.79 | 1.24 | 1.76 | 1.5 (0.3) |
| $m_{trapped}/m_0$ | 0.87 | 1.74 | 1.71 | 1.68 | 1.5 (0.4) |
| V_{total}/V_0 | 0.83 | 1.76 | 1.22 | 1.32 | 1.3 (0.4) |
| $V_{released}/V_0$ | 0.48 | 0.74 | 0.51 | 0.63 | 0.6 (0.1) |
| $V_{trapped}/V_0$ | 0.35 | 0.72 | 0.71 | 0.69 | 0.6 (0.1) |

The results summarized in **Table 4** indicate the following.

- Some portion of the oil is irreversibly trapped in the foam and cannot be released by simple squeezing. More oil would be removed by applying higher forces; however, it would damage the foam. The amount of permanently trapped oil does not significantly change during multiple cycles and remains roughly at the same level as after the first sorption step.
- The amount of the released oil does not depend much on the number of squeezing steps, and the average mass of the released oil is 1.5 ± 0.3 g/g. Approximately one-half of the absorbed oil can be released by pressing, and one-half is permanently retained.
- The amounts of absorbed oil, as well as the releasing and retaining portions, can be expressed in both weight fractions (mass of oil/mass of neat foam) and volume fractions (cm³/cm³). The total amount of absorbed crude oil in the weight fractions is $S_w = 3.0 \pm 0.7$ g/g, which is quite a low value compared with data for foamy, highly porous materials reported in the literature [1,18,19]. Many papers relating to the study of the sorption ability of porous materials refer to data for the S_w parameter in the range from tens to hundreds g/g [1,18,19], which may indicate little sorption ability of the *Qwax* foams in comparison with those data. However, the situation looks quite different if the comparison is performed for the volume of absorbed oil versus the volume of the foams. The total volume of absorbed oil per volume of neat foam is 0.83 cm³/cm³ in the first step, and the subsequent sorption cycles lead to values over unity (the average is 1.3 ± 0.4 cm³/cm³).

Finally, *Qwax* foam is a fully hydrocarbon-based structure. Nam et al. [24-27] pointed out the unique recycling advantage of their i-Petrogel sorbent, declaring that recovered oil/sorbent products containing no water can be directly refined the same as the original crude oil. On the basis of the chemical similarity of *Qwax* foam with i-Petrogel, *Qwax* foam saturated by crude oil would be recovered in the same manner in the final stage of its life cycle.

3.7. Comparison of the sorption ability of *Qwax* foam and commercial *PU* and *MA* foams

In this paragraph, we will examine the differences between S_w and S_v parameters in more detail. To compare the sorption abilities of *Qwax* foam with the most commonly used foams, such as extremely porous *MA* and *PU* foams (close to 99 vol% of pores), the sorption experiment was realized under the same conditions as for the sorption of *Qwax* foam. Similarly, as in the paragraph above, only the sorption of crude oil will be mentioned and discussed here. The sorption of diesel and motor oil behaved qualitatively in the same manner. The sorption ability of untreated *MA* and *PU* foams was tested using common sponges for daily use in kitchens for cleaning. Cubes with dimensions of 2x2x2 cm were cut and immersed into crude oil for six hours at room temperature. After six hours, the weight of the foams was recorded, and then foams were manually squeezed in a syringe into a maximum deformation. The mass of foam after squeezing and the mass of released oil were determined. Sorption for both foams immersed into crude oil was repeated ten times. The porosity of *PU* and *MA* foams (ϕ_p) was estimated from their specific densities according to the equation $\phi_p \approx 1 - \frac{Q_f}{Q_m}$ where ρ_f and ρ_m are the specific densities of foam and the skeleton material, respectively. The densities of foams were determined by the weight and the volume of foams (5x5x2 cm). The specific density of *PU* foam is 0.0287 g/cm³, and the specific density of *MA* foam is 0.0081 g/cm³. The specific densities of bulk (skeleton) materials may have different values depending on the real composition of thermosetting resins. Here, we use the values of 1.27 g/cm³ for polyurethane and 1.51 g/cm³ for melamine resin [53]. Then, the porosity of the *MA* foam was 0.995, and the porosity of the *PU* foam was 0.978. *SEM* micrographs of *MA* and *PU* foams are shown in **Fig. 11**, demonstrating the high porosity of both foams.

The comparison of sorption abilities of *MA*, *PU*, and *Qwax* foam is summarized in **Table 5**.

For the most commonly used parameter, S_w , *MA* foam shows the best performance, having a sorption ability of 59 g/g, followed by *PU* foam (23 g/g), and *Qwax* has a sorption capacity of only 3.1 g/g. The situation significantly changes if the volumes of absorbed oil are related to the volume of neat foams. In this case, the highest performance has *Qwax* foam having S_v equal to 1.3 cm³/cm³, followed by *PU* foam (0.69 cm³/cm³). The lowest value was found for the *MA* foam (0.59 cm³/cm³). Neither *PU* nor *MA* foams reached full saturation by crude oil, even after a long (six hours) immersion, which is probably caused by the blocking of pores. However, even if these foams are fully saturated, the S_v parameter can be maximally close to one due to the non swellable character of those foams.

The volume ratios indicate that the *Qwax* foam expands (swells) during sorption. From the measurements of the sample dimensions before and after the sorption experiment, it was found that the volume of *Qwax* foam increased to approximately 140% of its original volume. No volumetric changes were observed for *MA* and *PU* foams, as would be expected due to their rigid thermosetting structure. For multiple uses, an important parameter is how much oil can be released (by squeezing, in this case) in each cycle. If the mass ratio is considered, the sequence of efficiencies is the same as for the total sorption; however, the comparison of volume ratios indicates that *PU* and *Qwax* foam released almost the same amount of oil, whereas *MA* foam released the least volume of oil. These results confirm the considerations discussed above, namely, that the comparison of the sorption ability of foamy materials very strongly depends on what is compared - the weight or volume ratios. For the *Qwax* foam presented in this paper, the S_w ratio is very small in comparison with commercial foams, but the S_v ratio is the same or even higher than for those foams.

One of the drawbacks of *Qwax* against commercial *MA* and *PU* foams is its high retention of oil, which cannot be mechanically squeezed. Whereas commercial foams can release approximately 83% (*MA*) - 88% (*PU*) of absorbed oil, *Qwax* releases only approximately 50% of absorbed oil. A second drawback is the limited number of working cycles. On the other hand, the advantage of *Qwax* foam against

untreated *PU* and *MA wax* is negligible sorption of water. *PU* and mainly *MA* foams strongly absorb water and therefore need additional treatment to change their inherent hydrophilicity to induced hydrophobicity, whereas *Qwax* foam is inherently hydrophobic due to its nonpolar (hydrocarbon-based) character.

3.8. Characterization of the sorption capacity of highly porous foamy materials in terms of mass and volume

As shown above, the evaluation of the sorption ability of foams strongly depends on which unit is selected as the reference amount of the neat foam. The aim of this paragraph is to discuss it in more detail. The sorption capacity of foams can be characterized by two parameters -mass of absorbed oil per mass of neat foam (S_w) or volume of absorbed oil per volume of foam (S_v).

$$S_w \left[\frac{g}{g} \right] = \frac{m_{oil}}{m_f} \quad (4)$$

$$S_v \left[\frac{cm^3}{cm^3} \right] = \frac{V_{oil}}{V_f} \quad (5)$$

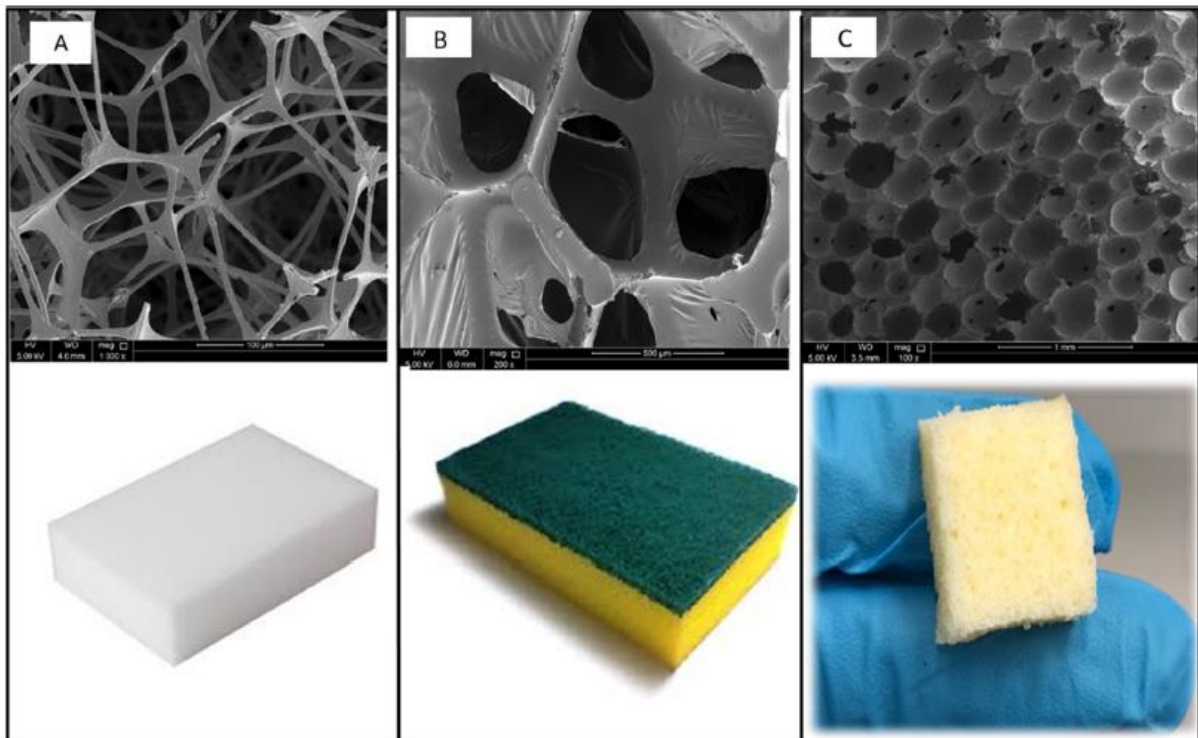


Fig. 11. Photographs and SEM micrographs of *MA* (A), *PU* (B), and *Qwax* (C) foams used for the sorption test.

Table 5 The parameters, which characterize the sorption ability of MA, PU, and Qwax foam.

| Foam | m_{total}/m_0 | $m_{trapped}/m_0$ | $m_{released}/m_0$ | V_{total}/V_0 | $V_{trapped}/V_0$ | $V_{released}/V_0$ |
|------|-----------------|-------------------|--------------------|-----------------|-------------------|--------------------|
| MA | 59 (2) | 10.0 (0.5) | 49 (2) | 0.59 (0.02) | 0.10 (0.01) | 0.49 (0.02) |
| PU | 23 (1) | 2.7 (0.3) | 20 (1) | 0.69 (0.03) | 0.08 (0.01) | 0.61 (0.04) |
| Qwax | 3.1 (0.7) | 1.5 (0.4) | 1.5 (0.3) | 1.3 (0.4) | 0.6 (0.1) | 0.62 (0.09) |

where m_{oil} and V_{oil} are the mass and volume of absorbed *oil*, respectively, and m_f and V_f are the initial mass and volume of neat foam, respectively. Let us consider non swellable foam created from skeleton material (m) with density ρ_m . Foam has a density ρ_f and porosity φ_p . Pores are filled by air (a density ρ_{air}). The foam absorbs a liquid, for instance, an *oil* with density ρ_{oil} . Let us also consider that oil is absorbed only in pores and neglects potential sorption in a skeleton. Then, Eq. (4) can be rewritten into Eq. (6).

$$S_w \left[\frac{g}{g} \right] = \frac{\rho_{oil} V_{oil}}{\rho_m (1 - \varphi_p) V_f + \rho_{air} \varphi_p V_f} \cong \frac{\rho_{oil} V_{oil}}{\rho_m (1 - \varphi_p) V_f} \quad (5)$$

where $m_{oil} = \rho_{oil} V_{oil}$, and $m_f \cong m_m = \rho_m V_m = \rho_m (1 - \varphi_p) V_f$ considering that the mass of the neat foam is equal to the mass of the material (*matrix*). The volume portion of *oil* ($\varphi_{p,o}$) can also be expressed by Eq. (6).

$$\varphi_{p,o} = \frac{V_{oil}}{V_f} \quad (6)$$

Then, Eq. (5) can be rewritten into Eq. (7).

$$S_w \left[\frac{g}{g} \right] = \frac{m_{oil}}{m_f} = \frac{\rho_{oil}}{\rho_m} \frac{\varphi_{p,o}}{(1 - \varphi_p)} = \frac{\rho_{oil}}{\rho_m} \frac{\varphi_p}{(1 - \varphi_p)} \text{ (for fully saturated foam)} \quad (7)$$

A limit case of sorption occurs when whole pores are filled with oil and foam is fully saturated. This represents the maximum sorption capacity of a foam (neglecting sorption in the internal structure of the material and no swelling, as defined above). Then, the volume portion of absorbed oil is equal to the volume portion of pores, and parameter S_w is given by the second term in Eq. (7).

Eq. (7) is shown in Fig. 12, where $\frac{\rho_{oil}}{\rho_m} = 1$ was chosen for the schematic depiction.

Fig. 12 demonstrates a huge nonlinearity of the parameter S_w [g/g] in the dependence on porosity (φ_p), and for highly porous foams, it reaches very high values.

The limit value of the parameter S_w can be calculated from the first term of Eq. (5) on the basis of simple consideration. In the limit case, we can consider the hypothetical foam that is formed by air only (hypothetically, we consider a closed volume element of air), and thus, ($\varphi_p \rightarrow 1$, and $p_m = p_{air}$). Then, S_w is given by a ratio of the density of oil and the density of air only, and $S_w^{limit} \approx \rho_o / \rho_{air}$.

For illustration, for selected oils (hexane, diesel, and crude oil), one can obtain limit values of S_w parameters of 544, 748, and 822 g/g, respectively (the oil densities used here are 0.655, 0.9, 0.99 g.cm⁻³, and 0.001204 g.cm⁻³ is the density of air at 20 °C, and normal conditions).

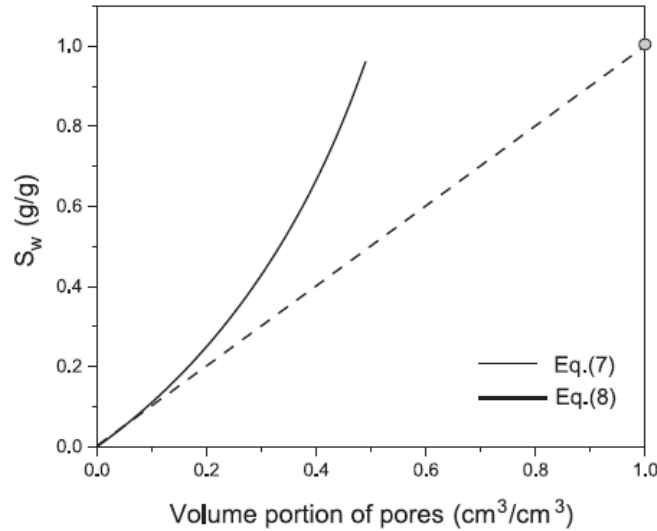


Fig. 12. The dependences of S_w and S_v on the volume portion of filled pores.

The second option is to express the sorption parameter (S_v) as a volume of absorbed oil (V_{oil}) per macroscopic volume of foam (V_f) according to Eq. (8). In the case of full saturation (whole pores are filled), the S_v parameter can be expressed by the second term in Eq. (8).

$$S_v \left[\frac{cm^3}{cm^3} \right] = \frac{V_{oil}}{V_f} = \frac{\varphi_{p,o} V_f}{V_f} = \varphi_{p,o} = \varphi_p \text{ (for fully saturated foam)} \quad (8)$$

Eq. (8) offers a linear dependence of an amount of absorbed liquid on the porosity in an object of finite volume. It enables a correct comparison of the sorption abilities of various sorbents and sorbates regardless of their chemical composition. On the other hand, parameter S_w is highly nonlinear and depends on the density of sorbents and sorbates, which complicates a mutual comparison of different sorbent-sorbate systems. It is intuitively clear that any quantity that physically correctly characterizes a sorption process should not depend on the densities of sorbents and sorbates but only on surface/volume-related parameters. Moreover, for non swellable foams, the parameter S_v directly characterizes the portion of filled pores in a foam. In the test performed in this study, it was found that only 69% of pores are filled by crude oil in the case of *PU* foam and 59% of pores in the case of *MA* foam. We suppose that the S_w parameter, which has a historical origin in the characterization of powder adsorbents, is less suitable for a comparison of the sorption capacity of various highly porous foams and membranes than parameter S_v . However, in a majority of scientific papers, only this

parameter pointed out the neglect of the importance of parameter S_v , which would enable a better comparison of the sorption behavior of different absorbents and sorbates.

4. Conclusions and future perspectives

The paraffinic waste product formed during industrial PE production was used for the preparation of foamy, elastic structures through crosslinking by dicumyl peroxide and foaming by 1,1'-azobiscarbamide. The porosity of the foam determined by computer microtomography was 58.9%, and the bulk density was $0.42 \text{ g}\cdot\text{cm}^{-3}$. The hydrophobic character of foam was observed under both air and oil, and the contact angle values of water were 114° and 128° , respectively. On the other hand, high oleophilicity was observed for *Qwax* foam under both air and water for all oils. The sorption ability of the foam was tested using diesel oil, motor oil, and heavy crude oil. The absorption capacity of foam was characterized as the ratio between the mass of oil absorbed by the foam and the mass of a neat foam (S_w) and as the ratio between the volume of oil absorbed by the foam and the volume of a neat foam (S_v). The absorption capacities of the *Qwax* foam were $6.6 \pm 0.3 \text{ g/g}$, or $3.3 \pm 0.2 \text{ cm}^3/\text{cm}^3$ for diesel oil, $3.9 \pm 0.4 \text{ g/g}$ or $1.9 \pm 0.3 \text{ cm}^3/\text{cm}^3$ for motor oil, and $3.4 \pm 0.2 \text{ g/g}$ or $1.4 \pm 0.4 \text{ cm}^3/\text{cm}^3$ for crude oil. It was found that the foam swells in oils and the initial volumes of testing samples increased by 138%, 30%, and 68% for diesel, motor, and crude oil, respectively.

To compare the sorption ability of *Qwax* foam with some common foams, the sorption capacities of highly porous, commercial polyurethane, and melamine foams were investigated under the same conditions. It was shown that these foams showed much higher sorption capacity considering the S_w parameter as a reference; however, the lower sorption capacity compared to parameter S_v . Testing of the sorption of crude oil revealed that *MA* foam showed the best performance if the S_w parameter was chosen as a reference, having a sorption capacity of 59 g/g, followed by *PU* foam (23 g/g). *Qwax* had a sorption capacity of only 3.4 g/g. The situation was utterly different if S_v parameters were compared. In this case, the highest performance was observed for *Qwax* foam with S_v equal to $1.4 \text{ cm}^3/\text{cm}^3$, followed by *PU* foam ($0.69 \text{ cm}^3/\text{cm}^3$). The lowest value was found for the *MA* foam ($0.59 \text{ cm}^3/\text{cm}^3$).

As mentioned in the introduction, *Qwax* foam has features similar to those of porous hydrocarbon-based materials called i-Petrogels. The main advantages of *Qwax* foam over i-Petrogel are i.) utilization of paraffin wax waste instead of pure polymers and monomers, ii.) simple crosslinking procedure without the need for organic solvents, iii.) no catalysts are needed, iv) no controlled metallocene polymerization must be performed, and v.) multiply used due to oil recovery by simple squeezing. The shortcuts are: i.) a smaller sorption capacity (g/g), and ii.) lower swelling ratio. However, regardless of the strategy of material preparation, polyolefin-like porous sorbents have great potential for oil remediation through the sorption of significant volumes of free oil. Future research will be oriented on the optimization of porosity with tuned open pores of appropriate size, reasonable mechanical strength, and mechanical stability in compression to perform more squeezing steps (over hundreds of cycles for *MA* and *PU* foams). The core problem seems to be an optimization of the degree of crosslinking. A high crosslinking density would lead to a significantly higher mechanical strength, improving the number of working cycles, but foam will be less swellable, as is common for highly crosslinked polymers.

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