Application of Shrimp Waste for the Synthesis of Polyurethane–Chitosan Materials with Potential Use in Sorption of Oil Micro-Spills in Water Treatment

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Abstract: Shrimp waste is a common waste in seafood processing. It is used as part of the fish meal which is added to feed. Bearing in mind the Green Deal and sustainability development, it was proposed to use northern prawn shells to obtain chitosan (Ch), which could then be used for polyurethane (PUR) modification. In ports, oil micro-spills often flow into the waters of gulfs and, consequently, into the sea. Systematic chemical and petroleum water pollution may pose a threat to flora and fauna. In this study, chitosan, which was obtained from shrimp shells, was used to synthesize polyurethane–chitosan foams (PUR+Ch) with different chitosan concentrations. Selected physico-chemical and sorption properties in relation to oil and water of these materials were determined. It was found that the amount of Ch added to the foam affected its morphology, hardness, density, and thermal and sorption properties. PUR foam with a 1.5% weight of Ch was characterized as having the highest water and oil sorption. The advantages of the tested material as an innovative product with potentially significant proecological values were estimated using strengths–weaknesses–opportunities–threats (SWOT) analysis. The conducted preliminary research made it possible to demonstrate the use of these materials in the processes of water treatment with the mentioned micropollutants.

Keywords: Green Deal; sustainable development; SWOT analysis; shrimp waste; chitosan; polyurethane foams; oil sorption; water sorption; eliminating pollution

1. Introduction

Climate change, environmental pollution, and environmental degradation are problems in Europe and in the world generally [1].

A total of 193 member states of the United Nations adopted the 2030 Agenda for Sustainable Development Goals on the 25 September 2015 in New York [2]. The agenda defines 17 Sustainable Development Goals and 169 related targets that should be achieved by the world by 2030. These goals aim to obtain achievements in five areas: people, planet, prosperity, peace, and partnership (the so-called 5xP). The goals cover a wide range of challenges: (1) no poverty; (2) zero hunger; (3) good health and well-being; (4) quality education; (5) gender equality; (6) clean water and sanitation; (7) affordable and clean energy; (8) decent work and economic growth; (9) industry, innovation and infrastructure; (10) reduced inequalities; (11) sustainable cities and communities; (12) responsible
consumption and production; (13) climate action; (14) life below water; (15) life on land; (16) peace, justice, and strong institutions; and (17) partnerships for the goals.

Nowadays, consumption of natural resources is extremely high and still increasing [3]. Air, water, and soil pollution are also increasing in many countries [3]. The 12th goal of the 2030 Agenda for Sustainable Development Goals concerns the assurance of sustainable consumption and production patterns [4]. The promotion of efficient use of energy and other resources is an important aspect of this goal. It aims to lower economic, environmental, and social costs via “do something better and more with less funds” [4]. A reduction in resource consumption, as well as the scale of pollution and environmental degradation, are capable of improving the quality of our lives.

Greenhouse gas emissions are constantly increasing [5]. Humans observe the severe effects of climate change, e.g., changing weather patterns, rising sea levels, and extreme weather events. Greenhouse gas emissions anywhere on earth affect people all over the world. Climate change is being felt in every country on all continents. The changes disrupt the development of national economies and threaten human health, society, and the environment. The 13th goal of the 2030 Agenda for Sustainable Development Goals concerns the urgent action needed to combat climate change and its impacts [6]. Appropriate minimization of the carbon footprint of new materials can have a positive effect on reducing greenhouse gas emissions [6].

The 14th goal of the 2030 Agenda for Sustainable Development Goals, which is essential to the water environment, aims to provide protection for ocean, sea, and marine resources, as well as their sustainable use [7]. Resolving the problem of polluted water and access to clean water are important for society [8]. Careful management of water resources is the key to a sustainable future for the environment and humans.

The plan to make the European (EU) economy sustainable is the European Green Deal [9]. The European Green Deal provides an action plan to (1) boost the efficient use of resources by moving to a clean, circular economy, and (2) restore biodiversity and cut pollution. It is a strategy that has the purpose of transforming the EU into a resource-efficient and competitive economy where there are no net emissions of greenhouse gases [10]. The project includes the following nine policy areas:

- Biodiversity (measures to protect our fragile ecosystem);
- From farm to fork (ways to ensure more sustainable food systems);
- Sustainable agriculture (sustainability in EU agriculture and rural areas due to the common agricultural policy);
- Clean energy;
- Sustainable industry (ways to ensure more sustainable, more environmentally respectful production cycles);
- Building and renovating (the need for a cleaner construction sector);
- Sustainable mobility (promoting more sustainable means of transport);
- Eliminating pollution (measures to cut pollution rapidly and efficiently);
- Climate action (making the EU climate neutral by 2050) [10].

Sustainable industry should include an economic policy based on the circular economy. The circular economy concerns the principle of closing the loop in a product’s life cycle [11]. The maximum use of a product’s potential should be related to its reuse (or its waste) after the end of its life cycle in the same cycle or a different new one. Circular economy phases are design (eco-design, resource saving, and product life cycle assessment), production (circular raw materials, process efficiency improvement, and by-product recovery), consumption (use, repair, and reuse), collection (waste storage in landfills and thermal waste treatment), and recycling (raw material recovery) [11,12].

The impact of water pollution on various branches of humans’ lives is well known, and concerns, for instance, the following:

- Urban and domestic use (increasing costs of water treatment);
- Human health (increasing costs of health treatment);
- Social values and tourism (threat to sailing, fishing, and bathing areas);
• Commercial fisheries (extinction of fish and contamination of shellfish);
• Ecosystem health (threat to flora and fauna);
• Industrial productivity (post-production water shortage);
• Agricultural productivity (water shortage after soil irrigation);
• Property values (adverse impact on the environment polluted in coastal areas).

The European Green Deal adopted a zero-pollution action plan to prevent the pollution of air, water, and soil. A reduction in particularly harmful pollution, e.g., microplastics, pharmaceuticals, oil, metal ions, and other contaminants, can result in the elimination of pollution from water. Sustainable use of chemicals in production in all industry sectors also provides a toxic-free water environment.

Shrimp waste is a seafood production waste in the food industry [12]. It is used as part of the fish meal which is added to feed. However, such utilization of this waste is a waste of valuable raw materials from natural sources. Bearing in mind the Green Deal and sustainability development, in this paper, we proposed the use of northern prawn shells to obtain chitosan (Ch), which was then used for polyurethane (PUR) modification. Managing the waste of other products in the design phase and production phase of a new material can be especially useful in a circular economy.

In ports, oil micro-spills often flow into the waters of gulfs and, consequently, into seas and oceans. The waters of the Baltic Sea are a currently very polluted, although the awareness of the dangers arising from this is extremely high. It is known that about 40% of pollution comes from the normal operation of vessels [13], despite the fact that activity is conducted in accordance with the principles imposed by the international conventions concerning the use of seas and oceans. Uncontrolled events (accidents, spills, and breakdowns) that cause contaminants to enter the water must not occur. However, a particularly high concentration of pollution is in the Gulf of Gdańsk, which is associated, among other things, with the activities of transshipment ports in Gdańsk and Gdynia in Poland [13].

It is obvious that there is a need to replace non-degradable traditional materials used in water treatment with biodegradable materials [14,15]. A few literature reports suggest that chitosan-based polyurethane may be an effective material for adsorbing metal ions [16], whereas polyurethane foams are used as oil spill absorbers [17]. We assume that the use of such a bifunctional material will increase the efficiency of water purification from such micropollutants.

In this study, chitosan, which was obtained from post-production of waste (shrimp shells), was used to synthesize polyurethane–chitosan foams (PUR+Ch) with different chitosan concentrations. Substrates used to obtain these materials (diisocyanate, polyol, and chitosan) are compounds that are biodegradable under conditions of a natural environment [18,19]. This guarantees that after the end of use of these foams, they will degrade without worsening the condition of the environment.

Selected physico-chemical properties and sorption properties in relation to oil and water of these materials were determined. It was found that the amount of added chitosan and the method of its addition to the foam affected the morphology of the foams, as well as their hardness, density, and thermal and sorption properties. This preliminary investigation made it possible to demonstrate the use of these materials in the processes of water treatment with oil micro-spills.

A strengths–weaknesses–opportunities–threats (SWOT) analysis [20] manages the assessment of the impact of the product on the environment and its innovative product properties. It is also a method that allows, for example, the estimation of the profitability of renewable energy [21,22] or the assessment of the socio-economic and environmental impacts of diminishing water resources [23,24], as well as the assessment of the threats and opportunities of mining enterprises [25,26]. A SWOT analysis can be an introduction to life cycle assessment from the perspective of sustainable development [27], and it is one of the tools in a circular economy [28].

2. Materials and Methods

2.1. Materials

2.1.1. Chitosan

Shrimp waste from northern shrimp (Pandalus borealis) was cleaned to separate carapace shells from the cephalothorax and abdominal segments from the abdomen. Then, chitin was extracted from the selected shrimp shells by subjecting them to (I) demineralization (9% HCl from 35–38% w:v, room temperature; 1.5 h); and (II) deproteinization (5% NaOH w:v, room temperature; 18 h). After each of the two steps, the sample was rinsed with tap water and distilled water until it was neutral. The shells were dried to dryness (80 °C; 16 h). Subsequently, chitin was converted to chitosan via chemical deacetylation (oil bath on a magnetic stirrer with mechanical stirring; 50% NaOH; w:v, 1:30; 130 °C; 3 h), the sample was rinsed to neutral and dried to dryness mass (80 °C; 18 h). The results of these processes are presented in Figure 1. The method of chitosan obtained from chitin is known in the literature [29–31].

2.1.2. Polyurethane–Chitosan Foams

The single-stage method and the two-stage method (so-called prepolymer method) of polyurethane foam synthesis are known in the literature [32]. The one-step method relies on all components to react in one step at room temperature. We chose the prepolymer method because one of the substrates of our synthesis (polyol) is solid at room temperature [18,19], hence the need to increase the synthesis temperature. In the first step of the prepolymer method, a diisocyanate was reacted with polyol at elevated temperature to obtain an isocyanate-terminated urethane prepolymer (in the presence of a suitable catalyst). In the second step, water with surfactant was added to the prepolymer (in the presence of suitable catalyst). Aliphatic isocyanate was selected for the synthesis because its degradation
products are non-toxic to the environment and human health, in contrast to aromatic isocyanates [18]. The used polyol is also biodegradable [19].

PUR+Ch were obtained by the two-step method, according to the modified procedure described in the literature [33]. The prepolymer was synthesized from a polyol (poly(ε-caprolactone) diol (PCL_diol), M_n 1900 g/mol, SIGMA-ALDRICH, St. Louis, MO, USA) and from diisocyanate (4,4′-methylene dicyclohexyl diisocyanate (H_{12}MDI), M_n 262 g/mol, SIGMA-ALDRICH, St. Louis, MO, USA) in tin(II) octanoate catalyst (OSn, ALFA AESAR, Karlsruhe, Germany) presence. All reagents were used as received.

The molar ratio of isocyanate to hydroxyl groups was 4:1. In the second step, a polyurethane (PUR) prepolymer was foamed with water and simultaneously modified with a biopolymer—Ch (1.5–3wt% of Ch in 1% acetic acid (CHEMPUR, Piekary Śląskie, Poland)) by intensive blending of both components in the presence of DABCO 33-LV (SIGMA-ALDRICH, St. Louis, USA) catalyst and TEGOSTAB B 8465 (EVONIK, Essen, Germany) as a silicone surfactant. The synthesis was performed as shown in the scheme (Figure 2):

The whole procedure for obtaining the foam consisted of 8 steps:

Stage 1: Dehydration of PCL_diol (vacuum; mixing 200 rpm; 100 °C; 3 h).
Stage 2: Preparation of the prepolymer by adding excess H_{12}MDI to the PCL_diol in OSn presence (vacuum; mixing 200 rpm; 100 °C; 3 h).
Stage 3: Mixing the obtained prepolymer with Ch in a 1% solution of acetic acid in water, DABCO 33-LV, and TEGOSTAB B 8465 (mixing; 1000 rpm; 60 s).
Stage 4: Storage of the sample in air at room temperature for 18 h.
Stage 5: Drying the sample in a vacuum oven at room temperature for 6 h.
Stage 6: Rinsing the sample by soaking it in a crystallizer with distilled water for 5 min.
Stage 7: Storage of the sample in air at room temperature for 18 h.
Stage 8: Drying the sample in a vacuum oven at room temperature for 12 h.

For comparison, a polyurethane foam without Ch (PUR) was also performed. Composition of PUR and PUR+Ch foams is shown in Table 1. The amount of acetic acid solution
was dependent on the amount of Ch, which was swollen in solvent. The photo of the synthesized foams is shown in Figure 3.

Table 1. Composition of PUR and PUR+Ch.

| Foam    | PCLdiol [g] | H$_{12}$MDI [g] | OSn [g] | Ch [wt%] | CH$_3$COOH (1% in Water) [mL] | DABCO 33-LV [g] | TEGOSTABB 8465 [g] |
|---------|-------------|-----------------|---------|----------|--------------------------------|-----------------|-------------------|
| PUR     | 15.010      | 8.234           | 0.045   | -        | 7.5                            | 0.075           | 0.282             |
| PUR+Ch1 | 15.044      | 8.334           | 0.045   | 1.5%     | 7.5                            | 0.075           | 0.270             |
| PUR+Ch2 | 15.009      | 8.261           | 0.045   | 1.5%     | 12.5                           | 0.075           | 0.280             |
| PUR+Ch3 | 15.020      | 8.209           | 0.045   | 3%       | 15.0                           | 0.075           | 0.273             |

Figure 3. Photo of synthesized foams (from the left): PUR, PUR+Ch1, PUR+Ch2, and PUR+Ch3.

2.2. Methods

2.2.1. Deacetylation Degree of Chitosan

Deacetylation Degree (DD) is one of the main parameters characterizing chitosan [34]. A few methods of DD determination of chitosan exist, e.g., analytical techniques and spectroscopy methods [29,34]. DD of Ch was estimated by the potentiometric titration method (PT), which is described in the literature [34].

DD value was calculated using the Equation (1) [34]:

$$DD\% = 2.03 \times \frac{(V_2 - V_1)}{m} + 0.0042 \times (V_2 - V_1)$$

where 2.03—coefficient resulting from the molecular of a chitin monomer unit; $V_1$, $V_2$—volumes of 0.1 mol/dm$^3$ sodium hydroxide solution corresponding to the deflection points; $m$—weight of a sample; and 0.0042—coefficient resulting from the difference between molecular weights of chitin and chitosan monomer units. The measurements of PT were repeated twice.

2.2.2. Molecular Weight of Chitosan

The number average molecular mass ($M_n$) and dispersity ($M_w/M_n$) were determined by gel permeation chromatography (GPC) [35] using a LaChrom liquid chromatographer (Merck-Hitachi) equipped with an L-7100 pump with the possibility of programming the liquid composition on the suction side, a Rheodyne 7725i dosing valve with a 100 µL dosing loop, an L-7350+ thermostat, a Knauer Smartline 2300 refractometric detector, and a computer with HSM-7000 software, version 4.1. There are three series-connected polyhydroxymethacrylate packed columns 300 × 8 mm. Eluent was 50 mM CH$_3$COOH + 0.3 M NaNO$_3$ with flow 0.65 mL/min. at temperature 35 °C. The volume of the dosed sample was 50 µL, about 0.01 g/mL concentration. Polystyrene standards with narrow molecular mass distribution were used to generate a calibration curve.
2.2.3. Chemical Structure

The samples of chemical structures were investigated by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), which was used to determine the characteristic groups of chitosan and polyurethanes [36,37]. FTIR spectra were recorded on a NICOLET 380 FTIR spectrometer (Thermo Scientific, Madison, WI, USA) with a diamond cell and attachment attenuated total reflection (ATR Smart Orbit Accessory, Thermo Scientific). A scanning range of 600 to 4000 cm\(^{-1}\) was applied with a resolution of 4 cm\(^{-1}\), and 32 scans were taken for each measurement.

2.2.4. Structure Morphology

A scanning electron microscope (SEM) is generally used to investigate the structure morphology of materials [38]. The sample surfaces were analyzed by a Quanta FEG 250 (FEI) SEM with an ET secondary electron detector. The images were taken at the samples cross-section and at the cross-section in multiple places to confirm sample uniformity. The acceleration voltage was constant and kept at 10 kV during the measurements.

2.2.5. Apparent Density

The apparent density of PUR and PUR+Ch materials was estimated via a gravimetric method, according to ASTM D3574-17 Standard Test Methods for Flexible Cellular Materials—Slab, Bonded, and Molded Urethane Foams [39], using analytical balance (RAWAG, Radom, Poland). The measurements of weights were repeated three times for each foam.

2.2.6. Hardness

Hardness of PUR and PUR+Ch foams was investigated using a digital hardness tester HD0 100-1 with Shore Hardness Scale 0, which is for foams and sponges (Sauter GmbH, Balingen, Germany). The measurements of hardness were repeated five times for each foam.

2.2.7. Thermal Properties

Thermal properties of PUR and PUR+Ch materials were determined using Differential Scanning Calorimetry (DSC) with the Setaram thermal analyzer (Setaram, Caluire, France). Indium and lead were used for calibration. Specimens (with mass about 10 mg) were sealed in aluminium pans and scanned from 20 to 200 °C, with the heating rate of 10 °C/min. All experiments were conducted in a flow of dry N\(_2\).

2.2.8. Sorption Properties

The sorption properties of PUR and PUR+Ch foams to oil and water were determined in accordance with ASTM F 726-99: Standard Test Method for Sorbent Performance of adsorbents [39]. A total of 3 cube samples with a base area of about 1 cm\(^2\) were cut out for each of the foams. Next, they were dried to dryness in a vacuum oven (37 °C; 3 h), weighed on an analytical balance (d = 0.1 mg), successively dried (37 °C; 1 h), and reweighed to verify the invariability of the mass value. A total of 120 mL of mineral diesel engine oil was poured into a 300 mL conical flask. Subsequently, the dried samples were immersed in oil and the sample was shaken (room temperature; 20 min). After this time, the foam samples were taken out and left on the filter paper for 30 s to drain excess oil, and then weighed. The samples were immersed in the oil again without shaking and left at room temperature for the daily measurement. One day after the first immersion, the samples were taken out and left on the filter paper for 30 s to drain excess oil, and then weighed. To check the regeneration of the samples after oil sorption, samples were rinsed with 120 mL of n-hexane by immersion in a solvent for 5 min and shaking. After this time, the samples were left on the filter paper for 30 s. The rinsing activities were repeated three times. After rinsing, the samples were left in the air at room temperature to evaporate the solvent. To check the efficiency of the regeneration of polyurethane samples, they were again subjected
to oil sorption after drying (to dry weight). The washing and sorption cycles were repeated twice (2nd and 3rd cycle).

The water sorption properties of PUR and PUR+Ch foams were investigated in the same way as for oil, but mass measurements were performed after 20 min, 1 day, 1 week, and 2 weeks, without sample regeneration.

Sorption was calculated (using the gravimetric method) from the weight after incubation \( w_i \) and the initial weight \( w_0 \) by the Equation (2):

\[
\text{Sorption [\%]} = \left( \frac{w_i - w_0}{w_0} \right) \times 100\% \tag{2}
\]

2.2.9. SWOT Analysis

SWOT analysis is generally a strategic planning technique that provides assessment tools [20]. SWOT analysis consists of the assessment of the internal factors: strengths (S), weaknesses (W), and the external factors: opportunities (O), and threats (T). SWOT can lead to fact-based analysis, fresh perspectives, and new ideas (also products).

To estimate the weights of individual factors, consisting of strengths, weaknesses, opportunities, and threats, the technique of binary comparison was used. The sum of weights within individual categories must be equal to 1.0. The grades of each factor were: 2—the lowest grade (the least important), 5—the highest grade (the most important). The choice of grade was made mainly in relation to the potential launch of the product on the market. To assess the strength of a factor’s impact on a given quadrant, we used the weighted scoring technique (factor weight \( x \) assessment of its impact). The calculation of the overall score for each quadrant (strengths, weaknesses, opportunities, and threats) allowed to determine what has the greatest impact on the tested materials.

The results of SWOT analysis could improve the use of natural resources, such as shrimp shells, and the influence of the product on its surroundings in accordance with human–nature interactions [18].

3. Results and Discussion

3.1. Deacetylation Degree of Chitosan

DD of Ch was determined by PT. The result of DD is shown in Figure S1 of the Supplementary Materials. Two titration steps are observed. The first step presents the neutralization of HCl, and the second step shows the amount of NaOH which was needed for the reaction with hydrogen cations on the amine groups of Ch. The calculation of the first derivative helps in an accurate reading of \( V_1 \) and \( V_2 \). The value of DD was made based on the Equation (1). In both measurements, the value of DD was similar and was equal to 75%.

3.2. Molecular Weight of Chitosan

Molecular weight of Ch was investigated by GPC. The value of molecular weight was 33,190 Da. The weight average molecular weight 117,225 Da \( (M_w) \), and the number average molecular weight was 33,190 Da \( (M_n) \). The polydispersity of Ch, i.e., the statistical dispersion of the mass of polymer molecules \( (M_w/M_n) \), was equal to 3.53. This value (above 2) points to a wider spread of mass.

3.3. Chemical Structure

Recording and analysis of the ATR-FTIR spectrum confirmed the obtaining of Ch. ATR-FTIR spectra of Ch, PUR, and PUR+Ch materials are shown in Figure 4.

In the spectra of Ch were observed the characteristic absorption bands attributed to the stretching vibrations of the \(-N-H\) and \(-O-H\) groups (at around 3275 cm\(^{-1}\)) and the symmetrical and asymmetric stretching vibrations of the \(C-H\) groups (at around 2872 cm\(^{-1}\)). It was also found that the intensity of the group bands corresponding to the stretching vibrations decreased for the amide I of \(-C=O\) group (at around 1646 cm\(^{-1}\)), for \(-C-N\) (at around 1312 cm\(^{-1}\)), and for \(-COC-\) group (at around 1149 cm\(^{-1}\)), as well as in stretching
vibrations of -CO groups (at around 1057 cm$^{-1}$ and 1016 cm$^{-1}$), in comparison to FTIR spectra of chitin. This indicated the deacetylation of C(O)NH$_2$ groups and the conversion of chitin into chitosan [36].

![Figure 4. ATIR-FTIR spectra of Ch, PUR and PUR+Ch.](image-url)

Figure 4. ATIR-FTIR spectra of Ch, PUR and PUR+Ch.

The presence of band characteristic in polyurethanes for PUR and PUR+Ch foams corresponding to the stretching vibrations of the -C=O group (at around 1728–1729 cm$^{-1}$) was found. These bands build an ester group in the structure of oligomerols (PUR soft segments) and together with the -N-H group with vibrations at around 3357 cm$^{-1}$ for PUR and at around 3346–3361 cm$^{-1}$ for PUR+Ch, form a urethane group -NHCOO-. Amide I band was observed at around 1729 cm$^{-1}$ for the investigated materials, while the peaks related to urea linkages were detected at around 1629–1631 cm$^{-1}$ (C=O stretching in urea) [40]. The amide II band was at around 1541 cm$^{-1}$ for PUR and at 1549–1550 cm$^{-1}$ for PUR+Ch foams. Shifting these bands towards higher wavenumber values may be due to the involvement of Ch molecules in bond formation.

Qin and Whang argue that a chemical reaction between these groups is possible to some extent [33]. However, in this research, chitosan on the PUR+Ch surface has not been found, even though the FTIR test was determined with an ATR. Thus, we suggest that chitosan has been trapped in the polyurethane matrix but has not built into its structure. Due to high steric hindrance, it was unlikely that a chemical reaction between the NCO group of diisocyanate and the OH group of chitosan would occur. Thus, the added chitosan acts as a filler and it reacts with PUR chains by hydrogen bonding.

The OH groups in the Ch structure were engaged in the formation of hydrogen bonds with the urethane group of PUR-Ch foams, which resulted in a shift in the -NH group band towards lower wavenumber values, from 3357.3 cm$^{-1}$ for pure PUR to 3345.7 cm$^{-1}$, 3352.3 cm$^{-1}$, and 3361.5 cm$^{-1}$, respectively, for PUR+Ch1, PUR+Ch2, and PUR+Ch3. The lack of shift of a band corresponding to the C=O group confirmed that hydrogen bonds must have arisen between the urethane groups of the hard PUR segments and the hydroxyl groups of the Ch.
All the bands of polyurethane found in the spectra of samples of PUR and PUR+Ch are typical for PURs [37,38].

3.4. Structure Morphology

SEM images (Figure 5) show a three-dimensional bubble structure of PUR and PUR+Ch foams. The pore diameters of the resulting foams were generally large and somewhat decreased upon incorporation of Ch into the PUR structure. A similar relation was stated by Qin and Wang [33]. Pore sizes in the PUR foam varied widely and their diameters ranged from 0.1 mm to 1.1 mm. The introduction of Ch resulted also in an increase in the uniformity of pore diameter. PUR+Ch foams have more homogeneous pores, with a size between 0.08 and 0.75 mm compared to PUR foam, and are slightly bigger than the size that is known in the literature [41]. However, adding more chitosan (3 wt%) to the PUR matrix did not improve the homogeneity of the pore diameter in comparison to foams with 1.5% chitosan content.

In addition to open pores, chitosan foams were characterized by the presence of much smaller closed pores (shown in the enlargement in Figure 5). This increased the sorption area in comparison to unmodified foam. Such a surface development in foams of PURs with Ch was also observed by Da Rosa Schio et al. [42].

3.5. Apparent Density and Hardness

The results of apparent density and hardness of PUR and PUR+Ch are presented in Table 2.

Table 2. Apparent density and hardness (with standard deviation SD) of PUR and PUR+Ch.

| Foam       | Density ± SD [kg/m³] | Hardness ± SD [° Shore H0] |
|------------|----------------------|-----------------------------|
| PUR        | 423 ± 72.7            | 36 ± 2.2                    |
| PUR+Ch1    | 415 ± 74.9            | 40 ± 1.5                    |
| PUR+Ch2    | 151 ± 18.8            | 18 ± 2.3                    |
| PUR+Ch3    | 434 ± 60.6            | 34 ± 0.6                    |
The apparent density of PUR, PUR+Ch1, and PUR+Ch3 ranged from 415 to 434 kg/m$^3$. These values are higher than normally rigid or flexible PUR foams (typically range from 30 to 100 kg/m$^3$) [43]. For extreme mechanical properties, the density of the PUR foam can even be increased to 700 kg/m$^3$ [44]. The addition of 1.5wt% Ch into the PUR foam (PUR+Ch1 and PUR+Ch2) reduced the density of the foam compared to the unmodified foam (PUR). This is unlike the highest addition of Ch (3wt% Ch in PUR + Ch3), which caused an increase in density. Javni et al. also showed that an increase in the concentration of filler in PUR foam caused an increase in foam density [44]. The porosity of a sample is inversely proportional to its apparent density. An increase in porosity (decrease in apparent density) should favor the sorption properties of the foams [40].

The hardness of PUR+Ch foams was lower than PUR. Generally, the addition of Ch reduced the hardness of the polyurethane material. Only the hardness of the PUR+Ch foam is slightly higher. The least dense and softest foam was PUR+Ch2. The higher amount of acetic acid needed to dissolve Ch in these conditions of synthesis was more appropriate.

3.6. Thermal Properties

DSC thermograms of all the foams showed two endothermic peaks connected to the PUR’s structure transformation (Table 3). The first peak related to the melting of the crystalline phase of polyurethane soft segments. Only in the case of PUR+Ch1 did the presence of chitosan particles in the PUR network disturb the arrangement of the soft segments and prevent their crystallization. For other PUR+Ch foams, the melting point increased slightly after introducing chitosan into the polyurethane matrix. At the same time, however, the melting enthalpy decreased. Thus, the resulting crystallites were probably slightly larger and better formed, but there were fewer of them. The second peak at 158.0–164.2 $^\circ$C ($T_{m2}$) related to the hard phase transformation that was connected with the change of order–disorder in the hard phase of polyurethane [45]. During heating, the hydrogen bonds dissociated in the hard phase. The enthalpy of this transformation ($\Delta H_2$) of the foams containing chitosan was much higher than in the case of pure PUR. The presence of chitosan changed the kinetics of the foam synthesis reaction. On this basis, it can be assumed that the observed differences in the enthalpy value of this transformation result from a different number of bonds formed in these materials, which is consistent with the observation of FTIR spectra.

| Foam     | $T_{m1}$ [°C] | $\Delta H_1$ [J/g] | $T_{m2}$ [°C] | $\Delta H_2$ [J/g] |
|----------|---------------|--------------------|---------------|--------------------|
| PUR      | 38.4          | 31.1               | 158.0         | 20.4               |
| PUR+Ch1  | -             | -                  | 163.7         | 47.0               |
| PUR+Ch2  | 41.0          | 19.2               | 160.1         | 59.2               |
| PUR+Ch3  | 44.2          | 20.0               | 164.2         | 54.4               |

3.7. Sorption Properties

The data presented in Figure 6 indicated that PUR+Ch absorbed more water than unmodified PUR. Pure PUR reached swelling equilibrium after 1 h of incubation in water. Meanwhile, PUR+Ch swelled throughout the test. The largest changes in the sample mass over time were observed for PUR+Ch2.

The presence of Ch, as a filler, in the polymer network of PUR caused an increase in hydrophilic properties. The highest changes in water sorption were observed after 1 and 7 days. The maximum adsorption capacity of foams after 14 days increased in PUR (48%), <PUR+Ch1 (121%), <PUR+Ch3 (164%), and <PUR+Ch2 (463%). The highest water sorption properties had PUR modified with 1.5%Ch (PUR+Ch2). PUR+Ch2 had more than 9.5 times better water sorption efficiency than PUR and was about 3 times larger than PUR+Ch foams. This value is higher than that of other PUR foams modified with natural
bio-additives [46,47]. This foam was also characterized by the lowest density and hardness among all the investigated materials. Increasing the amount of the water used to swell chitosan in the synthesis, in relation to PUR+Ch1, significantly influenced the structure of the PUR+Ch2 foam. The lower density facilitated the penetration of water molecules into this foam structure.

Li et al. also investigated PUR foams for oil spill cleanup [31]. Their results presented the water sorption capacity in the range from 51% to 141%. PUR+Ch3 and PUR+Ch2 had better properties. Oil sorption (Figure 7) was not a synergistic effect with water sorption for PUR+Ch3. The addition of 3wt% Ch to PUR reduced the apparent density of PUR. As in the case of water sorption, PUR+Ch2 with the highest porosity among all PUR+Ch had the best oil sorption properties. This indicated a higher influence of foam design features than its hydrophilic–hydrophobic properties on sorption.

After 20 min of incubation of the samples in diesel oil, the sorption did not exceed 100%. It was less than in the case of the foams prepared by Li et al. [39]. They presented the diesel sorption capacity in a range from 398% to 450%. However, in the first cycle of sorption, the maximum sorption capacity of the foams after 1 day of incubation increased in PUR+Ch3 (86%), <PUR; PUR+Ch1 (121%), and <PUR+Ch2 (467%). Estimation of oil sorption on the reused foams confirmed that the amount of sorbed oil gradually increased during the subsequent sorption cycles with PUR+Ch3 (109%), <PUR; PUR+Ch1 (124%), and <PUR+Ch2 (499%) in the third cycle of sorption after 1 day, which could indicate the migration of hydrophobic hard segments on the PUR surface under the influence of the oily medium. This may have a positive effect on their potential repeated use for water
treatment from oil micro-spills. Only the sorption of PUR+Ch3 samples after 20 min in the third cycle was extremely low. However, it increased after one day of incubation.

Figure 7. Oil sorption results.

3.8. SWOT Analysis

The theme of the SWOT analysis confirmed the impact of the studied materials on the environment, society, and economy (Figure 8).

Amongst strengths of the studied materials are the innovative value of the new products, the potential susceptibility of the studied materials for biodegradation in the natural environment after their use, the use of new products in the circular economy, and the new product signs in the Green Deal strategies and the 2030 Agenda for Sustainable Development Goals.

Polyurethane foams with chitosan have better sorption properties in relation to oil and water than unmodified materials. It is an enormous strength for the product before it is placed on the market, and for potential buyers.

Shrimp waste was used for the synthesis of PUR+Ch foams. Many tons of shrimp waste are produced. This waste presents a huge problem in the production of food from seafood. The industry has difficulties with its development. The use of this waste for feed meal is costly, with so much shrimp waste. At the same time, it is a loss of raw material that can be a source for obtaining a biopolymer, which is chitin. An example of our use of it could be used in a circular economy. It would be beneficial for the industry, the economy, and the environment.

The potential susceptibility of the studied materials for biodegradation in the natural environment after their use is important. An examination of the biodegradability of the studied materials after their end-of-life use is necessary. We plan to research this as soon as possible in the near future.

The production of more environmentally friendly materials for water treatment can have a positive impact on our surroundings. A cleaner environment improves people’s quality of life, and it is in accordance with the Green Deal strategy.
3.8. SWOT Analysis

The theme of the SWOT analysis confirmed the impact of the studied materials on the environment, society, and economy (Figure 8).

Nowadays, the market and society are interested in proecological and ecofriendly ideas [48]. Governments encourage citizens to buy and use ecofriendly products. These products contribute to the sustainable development of the environment and realize the 2030 Agenda for Sustainable Development Goals.

All these factors expose the innovative nature of these materials.

A weakness of the studied materials is a low efficiency of the chitosan production process on a laboratory scale and the preliminary stage of work on the tested new product. Determining the economic applicability of these materials would require a process (to obtain chitosan from shrimp waste) on a semi-industrial or industrial scale. Appropriate modification of the necessary equipment on a larger scale would certainly improve the efficiency of the process. It would be more efficient to obtain more chitosan in less time. An economic life cycle assessment of products could prove useful to estimate the difference in the production costs of PUR+Ch foams on a laboratory scale and a semi-industrial scale. This analysis should be carried out in order to fully assess the innovative value of the proposed product. Research on the use of chitosan in the production of polyurethane foams is still at the initial stage and requires advancement.

Actions for a sustainable economy in the EU and the elimination of petroleum pollutants in water treatment are opportunities for these materials and the environment.

An appropriate design of biodegradable materials prior to production should be required, e.g., eco-design. The use of chitosan derived from shrimp waste and biodegradable substrates for the synthesis of polyurethane foams were a favorable choice from an environmental perspective. Such action would be consistent with sustainable production and management. The amount of plastic waste and microplastic in the environment would be reduced. This phenomenon would minimize the negative impact of the environment...
on human health, flora, and fauna. It is consistent with the 14th goal of the 2030 Agenda for Sustainable Development Goals, which is to provide protection for oceans, seas, and marine resources, and use them in a sustainable way.

Legal bases for the EU’s policy in the field of environmental protection are included in the Treaty on the Functioning of the European Union [49]. It sets out the objectives and principles of this policy, covers decision-making procedures in environmental matters, and states that one of the objectives of the EU is to achieve the sustainable development of Europe, the dominant of which is environmental protection.

Mainly, the purposes of the EU’s policy on the environment includes the following:

- Preservation, protection, and improvement of the quality of the environment;
- Protection of human health;
- Cautious and rational use of natural resources;
- Promotion of measures at the international level to deal with regional or worldwide environmental problems, in particular combating climate change.

In the EU, the Eco-Management and Audit Scheme (EMAS) is also important. It is an environmental certification scheme that operates on the basis of Regulation (EC) No. 1221/2009 of the European Parliament and of the Council of 25 November 2009 on the voluntary participation of organizations in the eco-management scheme and community audit [50]. The EMAS is addressed to all types of organizations interested in implementing comprehensive solutions in the field of environmental protection. It is a useful tool for creating a culture of sustainable development and for the effective management of available resources and energy. The system is a reliable tool for reporting about environmental impacts.

The pollution of the waters of rivers, seas, and oceans is very dangerous. Legal regulations and proecological solutions contribute to the fact that companies and scientists are constantly investigating more efficient and more environmentally friendly materials which contribute to the elimination of various types of pollutants from water bodies. The studied materials show promising sorption properties towards oil.

Horizon Europe is the EU’s research and innovation framework program running from 2021–2027 [51]. One of the mission areas of this project is a healthy ocean, sea, coast, and inland waters. These areas are essential for our society and the future of our planet. They produce half of the oxygen which we breathe. They are also home to the richest biodiversity. The aims of this mission are systematic solutions for the prevention, reduction, mitigation, and removal of marine pollution, including oil, transition to a circular economy, and development of new materials, including biodegradable plastic substitutes. The possibility of obtaining external sources of financing for innovative proecological products to be used in water treatment processes with micropollutants is real.

Strong proecological social movements favor all activities (producers) related to environmental protection. These bottom-up activities are a significant support, as well as a kind of coercive measure for the rulers and producers to take into account the good of society and the protection of the natural environment in their policies and strategies.

Threats are related to weaknesses. Competition among companies producing materials with similar properties, and the global economic interests of industry sectors, are certainly threats. An economic life cycle assessment of products could prove whether the studied foams are economically beneficial for producers and buyers. Perhaps these results will be an opportunity or strength of these products which will allow us to overcome the existing threats.

Tables S1–S4 of the Supplementary Materials present the weight calculations performed using the binary comparison technique for individual factors of each quadrant. The calculation of the summary score for each group of factors (strengths, weaknesses, opportunities, and threats) allowed us to conclude that the strengths of the new product and the opportunities in the environment have the greatest impact (Table 4). Generally, this means that the proposed strategic option for the proposed innovative product is to enter the market with it, due to the existence of significant opportunities.
Table 4. SWOT analysis results.

| STRENGTHS                                      | Weight Grade | Weighted Scores | WEAKNESSES                                       | Weight Grade | Weighted Scores |
|------------------------------------------------|--------------|-----------------|--------------------------------------------------|--------------|-----------------|
| • Innovative value of the new products         | 0.10 5       | 0.50            | • Low efficiency of the chitosan production process on a laboratory scale | 0.70 4       | 2.80            |
| • Potential susceptibility of the studied materials for biodegradation in the natural environment after their use | 0.40 5       | 2.00            |                                                  |              |                 |
| • The use of new products in a circular economy | 0.30 5       | 1.50            |                                                  |              |                 |
| • The new products signs in the Green Deal strategy | 0.20 4       | 0.80            | • Initial stage of work on the tested new product | 0.30 3       | 1.00            |
| 1.00                                           |              |                 |                                                  | 1.00         |                 |

Summary assessment 4.80

| OPPORTUNITIES                                   | Weight Grade | Weighted scores | THREATS                                                      | Weight Grade | Weighted scores |
|------------------------------------------------|--------------|-----------------|--------------------------------------------------------------|--------------|-----------------|
| • Actions for a sustainable economy in the EU   | 0.20 5       | 1.00            | • Competition of companies producing materials with similar properties | 0.30 2       | 0.60            |
| • Legal regulations encourage to research new, innovative and proecological products | 0.27 5       | 1.35            |                                                              |              |                 |
| • Actions for elimination of petroleum pollutants in water treatment | 0.33 5       | 1.65            |                                                              |              |                 |
| • The possibility of obtaining external sources of financing for the studied materials | 0.13 4       | 0.52            |                                                              |              |                 |
| • Strong proecological social movements favoring all activities (producers) related to environmental protection | 0.07 4       | 0.26            | • Global economic interests of industry sectors              | 0.70 4       | 2.80            |
| 1.00                                           |              |                 |                                                              | 1.00         |                 |

Summary assessment 4.78

Summary assessment 3.80
The analysis shows that the basic strengths on which the future strategy of a new product should be built are the potential susceptibility of the studied materials for biodegradation in the natural environment after their use, and the use of new products in the circular economy. Focusing on the development of these two areas will allow us to take full advantage of the most important opportunities identified in the environment, i.e., actions for the elimination of petroleum pollutants in water treatment and legal regulations encourage us to research new, innovative, and proecological products. Thanks to this, the proposed product will become attractive to potential buyers, which will fit into the circular economy and fulfill its proecological mission. The effectiveness of the proposed actions will also require taking actions to minimize the impact of weaknesses and monitoring the environment in terms of threats [52].

In the literature, the SWOT analysis is known to present the future of materials [53]. The results of SWOT analysis of PUR+Ch materials indicate that attempts to use shrimp waste seem to be an important component in the development of new foams, which can be widely used for water treatment with micropollutants. The SWOT analysis is dominated by strengths and opportunities, which indicates that the implementation of new polyurethane–chitosan foams for production would be of great interest to customers (e.g., ports) due to their significant proecological and innovative value. SWOT analysis application of the test material for evaluation as a possible innovative product is an example of an interdisciplinary approach to this issue.

4. Conclusions

Sustainable consumption of natural resources and sustainable production that minimize the impact on the environment are an essential aspect of human life on earth. In the concept of a circular economy, shrimp waste can be used to obtain chitosan. Such a collection of this waste could probably be economically beneficial. Adding Ch to PUR improves the physicochemical and sorption properties of PUR+Ch. The synthesized materials were obtained from biodegradable substrates, which is a great advantage of reducing microplastics in a water environment. This fact ensures that, at the end of their service life, these foams will degrade without deteriorating the environment, which is due to the enormous amount of plastic rubbish lying on the earth. The best properties had PUR+Ch modified with 1.5wt% Ch, which was dissolved in 12.5 mL of acetic acid (PUR+Ch2). Furthermore, the results of the oil sorption properties of PUR+Ch2 foam are promising for their potential use in water treatment from oil micro-spills. The conducted SWOT analysis shows the advantages of the tested material as an innovative product with potentially significant proecological values. These aspects are important in the sustainable development of industry.

The oil sorption of the obtained foams is not high compared to other sorbents. However, a potential application of these materials is to trap oil micropollutants dispersed in water and metal ions. Both of these pollutants are found in the waters of ports and result from their normal operation. The high sorption of water suggests that the sorption of metal ions can also be high. This research will be the next stage of the research. The ability of oil micro-leakages sorption under dynamic conditions will also be tested, which is to determine whether the high hydrophilicity of these foams will allow the penetration of oil micro-spills into the foam structure.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su13095098/s1, Figure S1: An example of a titration curve and it is the first derivative in determining DD of Ch, Table S1: Estimating the weights of individual factors that make up the strengths, Table S2: Estimating the weights of individual factors that make up the opportunities, Table S3: Estimating the weights of individual factors that make up the weaknesses, Table S4: Estimating the weights of individual factors that make up the threats.

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