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Review

Research Progress on Oil−Water Separation Materials Based on Polyurethane Modification

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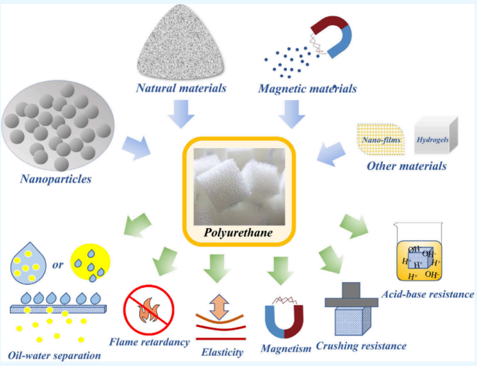
ABSTRACT: Numerous oil−water mixtures produced through industrial production processes and daily activities pollute the ecological environment and pose risks to human health. The development of materials with high oil−water mixture separation efficiency can promote the recycling of oil and water resources and effectively prevent environmental pollution caused by their direct discharge. Most of the current oil−water separation materials consist of foam, aerogel, and other porous materials. Among these materials, polyurethane exhibits good biodegradability, mechanical properties, large pore volume, low cost, wear resistance, and water resistance in oil−water mixture separation applications. However, pure polyurethane foam is characterized by low adsorption separation efficiency, insufficient recyclability, and high flammability. Therefore, modifying polyurethane to improve the oil−water mixture separation efficiency is vital. In this review, the methods and mechanisms of polyurethane modified materials used for oil−water mixture separation are reviewed, and their future research and application directions are prospected.



1. INTRODUCTION

The development of human society is closely linked to petroleum resources. However, in industrial production processes and daily life activities, the release of oil-based chemicals, industrial chemicals, and the massive discharge of oily sewage can cause severe water pollution, disrupt the ecological balance of water bodies, threaten human health, and lead to disastrous consequences for the aquatic environment and ecosystem.[1,2] Therefore, the efficient separation of oil−water mixtures has become a global issue. Generally, waterborne oil contaminants consist of insoluble hydrocarbons or fatty glycerides. Oil−water mixtures are classified into three main types, namely free-floating oil, unstable free oil droplets, and stable emulsions (with oil droplet diameters of <20 μm), according to their formation conditions.[3] Traditional oil−water separation technologies, including degreasing, adsorption, air flotation, centrifugation, and chemical coagulation, are characterized by low separation efficiency, high energy cost, complex operation process, and secondary pollution and can rarely separate highly emulsified oil-containing wastewate.[4,5] Chemical flocculation, high-voltage demulsification, and other methods can achieve demulsification. However, these methods are characterized by secondary pollution and high energy consumption, which limit their large-scale applications in oily sewage treatment.[6] With the rapid progress in material science, the research and development of oil−water separation materials with high separation efficiency, rapid separation speed, and high reusability remain an active and challenging research area. The main advantages of oil−water separation-based material separation over process-based separation mainly include efficient separation and purification, resource utilization, environmental friendliness, low cost and low maintenance.

Numerous materials are currently used for separating oil−water mixtures, such as poly(ether sulfone),[7] polysulfone,[8] polyvinylidene fluoride,[9] polyacrylonitrile,[10] and polyurethane (PU).[11] Among these materials, PU exhibits excellent advantages and has potential applications in oil−water mixture separation owing to its good biodegradability, biocompatibility, mechanical characteristics, large pore volume, low cost, wear resistance, and water resistance.[12] PU is a polymer synthesized through the reaction of multiple isocyanates and polyols and exhibits excellent physical and chemical properties.[13] However, pure PU foam or sponge has limited potential applications in oil−water mixture separation owing to its low adsorption separation efficiency, nondegradability, insufficient recyclability, and high flammability. Therefore, modifying PU through

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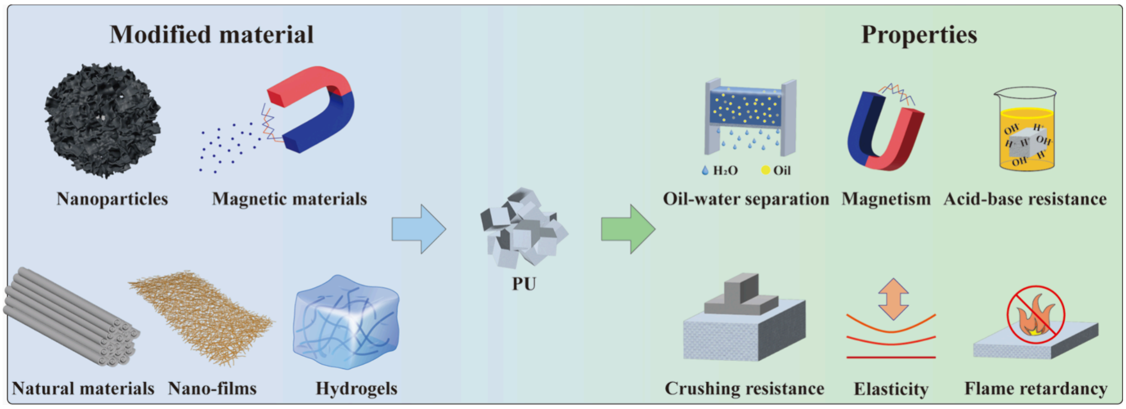

Figure 1. Oil−water separation materials based on PU modification. The separation efficiency of oil/water mixture, flame retardancy, elasticity, magnetism, crushing resistance and acid and base resistance were improved by modifying PU with nanoparticles, natural materials, magnetic materials, and other materials.

various methods and strategies to enhance the efficiency of oil−water mixture separation and broaden its application range is vital. The main advantage of PU based-materials in oil−water separation applications is their controllable hydrophilic−hydrophobic conversion function, which enables PU based-materials to achieve the transition between hydrophilic and hydrophobic properties under different environmental stimuli, so as to be suitable for oil−water separation processes in complex environments. In contrast, other polymers, such as poly(ether sulfone), may not have this controlled affinity-hydrophobic conversion, or may be more complex or less efficient to implement. At present, the core mechanism of PU-based oil−water separation materials is based on the controllable conversion of their surface wettability, so as to achieve selective separation of oil−water mixtures This PU-based modified material is often characterized by super-hydrophobic, superlipophilic or superhydrophilic superoleophobicity, enabling the transition between hydrophilic and hydrophobic properties under different environmental conditions, thus being used in complex oil−water separation processes. Specifically, PU-based oil−water separation materials are chemically modified and physically designed to give their surfaces specific wettability. Presently, PU modification mainly includes nanoparticle modification, natural material modification, and magnetic material modification (Figure 1). In this paper, the main methods and mechanisms of PU-modified materials used for oil−water mixture separation are reviewed.

2. PU MATERIALS MODIFIED WITH NANOPARTICLES FOR OIL−WATER SEPARATION

Nanoparticles exhibit unique advantages in material modification due to their unique physicochemical properties.[14,15] It has been proven that surface modification of materials with nanoparticles can regulate their surface roughness,[16] surface hydrophobicity,[17] mechanical characteristics,[18] optical and thermal properties,[19,20] and so on. Among them, the use of different nanomaterials to modify PU to improve its efficiency in oil−water separation processes have also been widely studied, such as the use of silica nanoparticles and carbon-based nanomaterials (Figure 2).

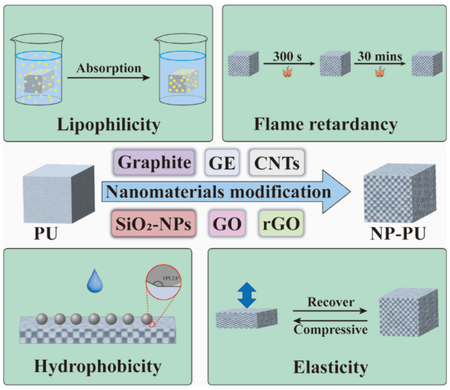

Figure 2. PU material modified by silica nanoparticles, GE, GO, rGO, and CNTs to improve its lipophilicity, flame retardancy, hydrophobicity, and elasticity during the oil−water separation process. NP-PU represents the PU material modified by nanoparticles.

2.1. PU Materials Modified with Silica Nanoparticles.

The main text of the article should appear here with headings as appropriate. Unprocessed PU has demonstrated specific hydrophobic properties. To further enhance the oil−water separation ability of PU, Wang et al.[21] attempted to improve the surface roughness by introducing composite nanoparticles onto the PU surface to achieve superhydrophobicity. Batool et al.[22] prepared a PU nanocomposite fiber film-containing silica nanoparticles (SiO_2−NPs) through electrospinning and electrospraying processes, resulting in a film with good permeability, mechanical, and chemical stabilities, which is suitable for achieving both oil−water separation and self-cleaning purposes. This study indicates that the structure of the composite film can be regulated by varying the concentration of SiO_2−NPs and PU. For example, the surface roughness and layered structure of the composite film can be regulated through the adjustment of the parameters of electrostatic spraying. The resulting composite membrane exhibited good mechanical characteristics and a large water contact angle of 155.23°, demonstrating its superhydrophobic ability. Moreover, Batool et al.[22] found that the composite nanofiber membrane featured significant water/oil separation efficiency and achieved separation rates of 99.98%, 99.97%, and 99.98% for water/xylene, water/*n*-hexane, and water/toluene mixtures, respectively. Yuan et al.[23] used SiO_2−NPs to modify a PU film and in situ cross-linked SiO_2−NPs with PU using a silane coupling agent (KH550) to produce a well-dispersed enhanced PU film. The water contact angle experiment confirmed that the PU film featured a contact angle of 90.71° after treatment

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with the silane coupling agent. With increasing SiO_2−NP concentration, the water contact angle of the SiO_2−NP/PU film gradually increased (from 94.13° to 103.90°). In addition, the oil−water separation experiment confirmed that the membrane containing 15% SiO_2−NP/PU effectively separated the mixture of Sudan III and water and exhibited good recyclability.[23] In addition, a study has been conducted to achieve efficient and economical oil−water separation by coating superhydrophobic SiO_2−NP on the surface of polyurethane.[24]

Owing to its high viscosity, crude oil is not easily absorbed by foam at room temperature. However, Ma et al.[25] found that the viscosity of crude oil rapidly decreased with increasing temperature. As crude oil droplets with reduced viscosity are heated to 60 °C and introduced to the foam surface, they can be completely absorbed into the foam within 5 s. To improve the adsorption and separation efficiency of the PU film on crude oil, Wu et al.[26] incorporated 1H, 1H, 2H, 2H-perfluorooctane trichlorosilane-modified SiO_2 (F-SiO_2) into lignin-containing PU foam to prepare an adsorbent with good oil−water separation, adsorption, and degradation properties. Water contact angle experiments revealed that the lignin-containing PU foam modified with F-SiO_2 featured superhydrophobicity and a water contact angle of 151.3°. After 100 cycles of compression, cutting, and wear, the water contact angle of the PU foam remained significantly unchanged, and the oil−water separation efficiency reached 99%. The photothermal conversion property of lignin endowed the composite PU foam with the capacity to absorb crude oil, resulting in a rapid increase in the surface temperature to 77.6 °C under simulated light irradiation of 1 kW/m^2. After immersing the prepared F-SiO_2-modified PU foam containing lignin in an alkaline alcohol solution for 2 h, nearly all of the foam degraded, possibly owing to the cleavage of ether bonds in lignin caused by the alkaline solution. The degradation of SiO_2 was attributable to the reaction between SiO_2 and NaOH to produce sodium silicate and water.[26] Recently, Wang and colleagues[27] developed a concise method to prepare stable superhydrophobic oil−water separation materials. In this work, a thermoplastic PU foam was modified by combining phase separation technology and silica coating. The results confirm that the water contact angle of the modified thermoplastic PU reaches 155.62°, and the maximum saturated adsorption reaches 54.11 g/g.[27] The modified thermoplastic PU is used in 10 filtration cycles to maintain a consistent separation efficiency. Moreover, there are also studies on the use of fluorinated compounds to reduce the surface energy characteristics of SiO_2−NPs to modify the PU foam with high-efficiency oil−water separation of fluoroalkylsilane-modified silica nanoparticles fixed.[28] Therefore, combining silica with PU through different methods and strategies can effectively improve the hydrophobic ability of PU and improve its oil−water separation efficiency.

2.2. PU Materials Modified with Carbon-Based Nanomaterials. Graphite (GE), graphene oxide (GO), reduced graphene oxide (rGO), and carbon nanotubes (CNTs) exhibit low surface energy and can aggregate to form rough layered micro/nanostructures, which is a vital requirement for constructing superhydrophobic surfaces.[29] Therefore, to further improve the oil−water separation efficiency of PU, numerous studies have modified PU with carbon-based nanomaterials including CNTs, GO, and rGO.

2.2.1. Carbon Nanotubes (CNTs). CNTs are used to create superhydrophobic surfaces owing to their inherent hydrophobicity, high adsorption capacity, low density, and strong mechanical properties.[30] At present, there have been studies to improve the superhydrophobic and superlipophilic abilities of PU by combining CNTs with polyurethane by means of a dip coating[31] and chemical reactions.[32] Shan et al.[33] found that incorporating CNTs into various superhydrophobic materials enhanced their mechanical durability, chemical and thermal stability, and flame retardancy. For example, Chen et al.[34] prepared superhydrophobic CNTs by introducing long-chain hexadecylsiloxane groups into hydroxylated multiwalled carbon nanotubes (MWCNTs). Subsequently, they fabricated materials with oil−water separation properties by integrating the modified CNTs with an oil-wet PU sponge through an impregnation coating method. The results revealed that the PU sponge modified with MWCNTs exhibited excellent superhydrophobic properties, with a water contact angle of 157.4 ± 1.1°, and featured excellent adsorption capacity for different oils and organic solvents. Liu et al.[35] discovered that modifying PU sponges with MWCNTs improved their hydrophobicity. Compared with unmodified PU sponges, PU sponges modified with MWCNTs featured increased water contact angles from 64.1° to 151.3°. This enhancement improved the oil adsorption capacity of PU sponges and increased their mechanical strength. Thermogravimetric analysis revealed that the thermal stability of the PU sponge modified with MWCNTs increased from 3.5% to 55% at 500 °C.

Considering that the recovery of oil spills in a multimicrobial marine environment requires not only high adsorption properties but also efficient antimicrobial properties, some studies have been conducted to prepare materials with both antibacterial and efficient oil−water separation by adding amino acids to PU and then modifying MWCNTs with dopamine.[36] The modified PU allows for cyclic adsorption while preventing bacterial adhesion. In addition, there are also studies on the use of multiwalled carbon nanotubes combined with metal−organic frameworks to modify polyurethane foams to make them have the ability to have strain/pressure sensors and efficient oil−water separation capabilities.[37]

2.2.2. Carbon Nanofibers and Nanodiamonds (NDs). In addition to using CNTs to improve the hydrophobicity and mechanical characteristics of PU sponges, Visco et al.[38] demonstrated that loading carbon nanofibers onto the PU foam improved its hydrophobicity, mechanical properties, oil−water separation ability, and repeatability. The results indicated enhanced hydrophobicity (with a water contact angle of 111−114°) and improved lipophilicity of the composite PU foam. The fatigue test results show that the elastic behavior of the foam increases with the increase of carbon filler, which achieves a related improvement in the long term mechanical properties of the foam. The presence of carbon nanofibers causes the sponge structure to harden and increases the energy per unit volume absorbed during load application. In addition, the composite PU foam exhibited a 22.85% increase in its selective oil absorption in mixed water/oil media. Furthermore, nanodiamonds (NDs), as one of the most promising new carbon-based materials, have been used to improve the oil−water separation ability of PU. Cao et al.[39] used the strong adhesive property of polydopamine (PDA) to coat hydroxylated NDs with PDA and then reacted them with 1H, 1H, 2H, 2H-perfluorooctane trichlorosilane. Owing to the excellent bonding ability of PDA, the modified NDs were firmly fixed to the skeleton of a commercial PU sponge. Scanning electron microscopy showed strong agglomeration of NDs-fPDA powder. PU sponges exhibit a three-dimensional layered structure composed of irregular pores that uniformly agglomerate NDs-fPDA particles distributed on PU fibers. Moreover, the prepared PU sponge exhibited superhydrophobicity (with a water contact angle of 160°), excellent oil−water separation performance, and a high organic adsorption capacity.

2.2.3. Graphite (GE), Graphene Oxide (GO), and Reduced Graphene Oxide (rGO). Expanded graphite is a loose and porous wormlike material obtained from natural graphite flake through a process involving intercalation, washing, drying, and high-temperature expansion. In addition to the excellent properties of natural graphite such as cold and heat resistance, corrosion resistance, and self-lubrication, expanded graphite features unique properties such as softness, compression resilience, and adsorption compared with natural graphite.[40] Vasquez et al.[41] used two solvent-free manufacturing processes to produce foam with different pore sizes for the oil−water filtration process. In the first method, expanded graphite particles were mixed with water-based PU, while in the second method, calcium carbonate was introduced into the two-component mixture. In both cases, the resulting foams exhibited hydrophilic and lipophilic behavior in the air and oleophobic behavior in water and featured porous interconnected networks with significantly varying pore size distributions. The prepared foam served as a three-dimensional filter for the efficient gravitational separation of surfactant-free oil-in-water mixtures (with 10% w/w oil-in-water) with high degreasing efficiency and flow rates.

GO is an oxygen-rich material produced through the controlled oxidation of graphite and exhibits an extended layered structure, with hydrophilic polar groups (hydroxyl, carboxyl, and epoxy groups) protruding from its layered structure, resulting in swelling and ion exchange properties. Owing to its low cost, chemical stability, and environmentally friendly properties, GO has received great interest in recent years. Although GO is hydrophilic, rGO is derived from GO through the removal of some polar functional groups on GO during the reduction process.[42] Liu et al.[43] coated a PU sponge with an rGO thin layer to obtain an rGPU sponge for absorbing various organic liquids, including diesel, pump oil, lubricating oil, olive oil, soybean oil, chloroform, and toluene. Owing to the rGO coating, the rGPU sponge exhibited a high-water contact angle of 127°, good hydrophobicity, lipophilicity, and strong compressive strength. Hao et al.[44] found that immersing PU sponges with a hollow tube structure in rGO increased the adsorption capacity of the PU sponges for various oils, ranging from 21.7−55 g/g. In addition, Chen et al.[45] incorporated 3% rGO into a porous thermoplastic PU sponge to improve its hydrophobicity and mechanical properties. The morphological results revealed that the three-dimensional composite sponge exhibited a uniform distribution of micropores and nanopores and featured hydrophobicity (with a water contact angle of 114°) and improved mechanical properties. The composite exhibited remarkable superelasticity, excellent reversible compressibility, and fatigue resistance (with a strength of 186 kPa at 80% strain), which enabled it to reabsorb oil through simple manual extrusion, thereby improving its application prospects.

One drawback of PU sponges is their high flammability owing to the large surface area exposed to react with oxygen, which can lead to ignition during the separation/transportation of flammable liquids (such as crude oil).[46,47] To address this shortcoming of the PU sponge, GE and rGO were used to improve the oil−water separation efficiency and fire resistance of PU. For example, Zhang et al.[48] prepared a superhydrophobic PU sponge modified with thiolated GE. The modified sponge maintained an oil−water separation efficiency of 99.7% after five regeneration cycles. Modified PU sponges can absorb various oils and organic solvents, which increased their mass by 90 times their original amount. The presence of GE in the coating endowed the modified superhydrophobic nanohybrid sponge with flame retardant properties, which reduced the combustion hazard during the collection/transportation of the separated oil. In addition, Chen et al.[49] prepared a superhydrophobic flame-retardant nanohybrid PU sponge through the synergistic effect of PDA and rGO. The presence of catechol in PDA inhibited free radicals generated during degradation, while rGO served as a physical barrier by impeding the transport of heat, oxygen, and volatile products. Considering the difficulty of separating a large number of various organic pollutants and inorganic pollutants in water, Sahu et al.[50] recently modified PU with rGO nanosheets to achieve efficient separation of different organic oils and heavy metals. The superhydrophobicity and superoleophilicity of rGO modified PU were confirmed by a high-water contact angle of about 164° and low oil contact angle of about 0°, respectively. Considering the good photothermal effects of graphene and its derivatives, Ji and colleagues[51] modified the surface of the PU sponge with dopamine and GO, and then reduced it using a constant temperature hydroiodic acid solution at 65 °C. The water contact angle of the composite polyurethane material prepared by this simple method can reach 155°, showing the characteristics of superhydrophobicity and superlipophilicity, and the material has high adsorption capacity for light oil and crude oil, and has strong photothermal influence.

In addition to the previously mentioned CNTs, GE, GO, rGO, the use of carbon black (CB) modified PU to improve its separation efficiency in high-viscosity crude oil has also been reported recently. For instance, Wang et al. used low-cost PU sponges, CB nanoparticles and fluorinated silane coupling agents (FAS) as raw materials to prepare superhydrophobic PU/CB@FAS sponges with photothermal effects by dip coating method.[52] The results show that the photothermal conversion performance of PU/CB@FAS sponge at 1 sun (1.0 kW/m^2) optical power density is 15 times higher than that of the nonlight condition. Another study used polydimethylsiloxane (PDMS)/CB to modify PU sponges by a simple one-step dip-coating method.[53] The maximum surface temperature of the modified PU sponge can reach 84.7 °C under 1 sun irradiation. The modified PU sponge can rapidly heat and enhance the fluidity of viscous crude oil, significantly speeding up the viscous oil recovery process with the maximum adsorption capacity of 44.7 g/g.[53]

3. PU MATERIAL MODIFIED WITH NATURAL MATERIALS FOR OIL−WATER SEPARATION

3.1. Halloysite Nanotubes and Sepiolite. To enhance the oil−water separation efficiency of the PU foam or sponge, improve its reusability, simplify its manufacturing process, and promote its large-scale application, several studies have explored the use of natural clay and diatomite to modify PU (Figure 3). Halloysite nanotubes are natural tubular clay with a

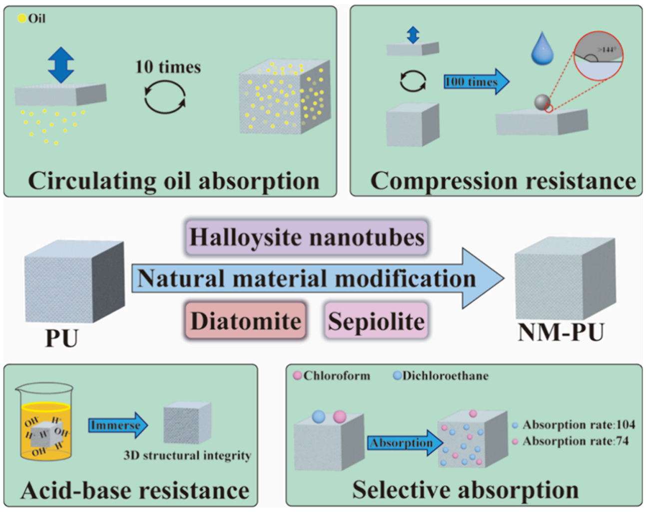

Figure 3. PU material modified with halloysite nanotubes, sepiolite, and diatomite to improve its circulating oil absorption capacity, resistance to highly acidic and alkaline liquids, and selective adsorption capacity during the oil−water separation process. NM-PU represents the PU material modified by natural materials.

diameter of 50 nm, a specific surface area of 60−70 m^2/g, and an adjustable surface chemistry. Nanoclays exhibit numerous advantages, including being obtained without a peeling process, a high aspect ratio, thermal stability of 1200 °C, good mechanical strength, a well-developed pore structure, and satisfactory stable water dispersion, which allowed for various surface modifications.[54] Halloysite nanotubes exhibit a hydrophilic state that can be transformed into a hydrophobic state through hexadecyltrimethoxysilane and tetraethoxysilane condensation reactions.[55] Furthermore, Wu et al.[56] modified a PU foam by dipping and coating it with strong hydrophobic halloysite nanotubes to obtain a superhydrophobic PU foam. The superhydrophobic PU foam exhibited a water contact angle of 150°. The modified PU foam exhibited highly selective absorption of oil and organic solvent, with absorption rates of 104 and 74 for chloroform and dichloroethane, respectively. This superhydrophobic foam maintained oil absorption performance even after 10 absorption−extrusion cycles, exhibited good recyclability, and could continuously and rapidly absorb oil or organic solvents from the water surface.[56]

Sepiolite ($Mg_8(OH)_4S_{i12}O_{30}{\cdot}nH_2O$) is a natural clay mineral that is nontoxic and environmentally friendly. On the sepiolite surface, numerous silanol groups react with organic coupling agents to prepare various functional materials. Recently, Pang et al.[57] modified fibrous sepiolite by depositing silica on its surface through a sol−gel process, followed by a reaction with 1H, 1H, 2H, 2H-perfluorooctane trichlorosilane. Superhydrophobic sepiolite/silica was firmly attached to the surface of the PU sponge under the action of oily epoxy resin, with strong adhesion. The modified PU sponge featured superhydrophobicity and excellent selective oil adsorption capacity (from 19.98 to 40 times its weight). More importantly, in addition to effectively separating immiscible oil−water mixtures (with a separation rate of 98.72%), the modified PU sponge can also effectively separate oil from water and salt solution emulsions. In addition, PU sponges maintained their hydrophobic properties even after floating in extremely corrosive liquids for 20 h and featured strong resistance to strongly acidic and alkaline solutions. After undergoing 100 cycles of mechanical compression, the three-dimensional structure of the sponge remained unchanged, and its water contact angle exceeded 144°. This indicates excellent mechanical stability, which provides valuable insights for the practical application of the sponge in oil−water separation.[57]

3.2. Diatomite.

Oil−water emulsion is an oily wastewater commonly found in daily life and industrial production and requires treatment before discharge. In traditional processes, the oil−water emulsion is susceptible to oil pollution and blockages, resulting in increased operational energy consumption and demulsifier costs. Frequent replacement of adsorbents further hinders cost-effective and efficient emulsion treatment. In response to this issue, Wu et al.[58] fabricated a PU/diatomite composite material with superamphiphilic and superamphiphobic properties to achieve rapid demulsification in a fluid environment through vacuum pumping. In this study, an oil−water separator with a superhydrophobic double-layer corrugated channel structure was connected to a suction filter device through a peristaltic pump to form a demulsification separation device, which can achieve a 99.5% emulsion separation efficiency. This study found that the hydrostatic contact angle (WCA) and oil contact angle (OCA) were 69 ± 4° and 3 ± 1° for the pristine diatomite and 56 ± 3° and 11 ± 2° for the dried PU glue. However, both WCA and OCA of PU/diatomite composite are 0°, indicating that superamphiphilicity was obtained by combining the hydrophilic/oleophilic raw materials. The demulsifier with PU/diatomite as the core material can stably separate the oil−water emulsion. The water-in-oil emulsion and oil-in-water emulsion remained stable over a prolonged time under constant vacuum pressure and flow rates, and the separated water and oil can be regarded as discharge wastewater and recyclable oil, respectively.

3.3. Lignin and Chitosan.

In addition, bioderived natural materials such as lignin and chitosan are also used to modify polyurethane to improve its oil−water separation efficiency.[59,60] A novel photothermal superhydrophobic lignin-based PU foam adsorbent was prepared by one-step foaming process.[59] In this study, PU foams with superhydrophobic and photothermal characteristics were prepared by mixing F-SiO_2 and lignin liquefied in polyols through one-step mixing foaming technology. The lignin-based PU foam with F-SiO_2 had a superhydrophobic water contact angle of 151.3° and the efficiency for oil−water separation reached 99%. In addition, the lignin-based PU foam with F-SiO_2 exhibited self-cleaning properties and degraded within 2 h in an alcoholic alkali solution.[59] In addition to the use of lignin to modify PU, there are also recent studies exploring the use of chitosan to modify PU to improve its oil−water separation ability. MohammadAlizadeh and Elmi[60] immersed PU in a PDA/chitosan-g-octanal solutions to prepare a thermostable, superhydrophilic, and superhydrophobic material. The maximum sorption capacity for olive oil of the modified PU materials was found to be as high as 41.48 g/g. And the modified PU has good flame retardancy and the ability to quickly extinguish the flames, which is very important for adsorption with crude oil.[60]

4. MAGNETIC MATERIAL MODIFIED PU MATERIAL FOR OIL−WATER SEPARATION

To further improve the oil−water separation efficiency of PU foam or sponge, several researchers have explored the development of PU materials with a magnetic response (Figure 4). Currently, one common approach involves incorporating magnetic nanomaterials into PU through various

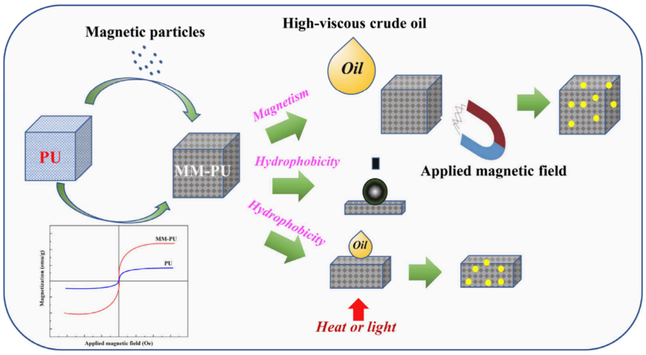

Figure 4. PU material modified with magnetic nanomaterials to improve superhydrophobic capacity, thermal conductivity, and promote the fluidity and efficient absorption of crude oil. MM-PU represents the PU material modified by magnetic material.

processes to impart magnetic properties. For example, Calcagnile et al.[61] prepared superhydrophobic and oleophilic PU sponges with magnetic properties by incorporating superparamagnetic iron oxide nanoparticles into PU sponges and then modifying them with submicron polytetrafluoroethylene particles. The resulting magnetically responsive PU sponge exhibited a water contact angle of 160° and could rapidly adsorb oil from the water surface using a magnetic field. The manufacturing technique is simple and suitable for large-scale production and utilizes low-cost materials, with recycling potential. The PU sponge effectively removed large amounts of oil from water using magnetic fields to propel superparamagnetic, water-repellent, and oil-absorbing foam toward the contaminated area from a distance with minimal energy consumption.[61] The key method for preparing magnetic superhydrophobic PU sponges involves attaching magnetic particles to porous PU sponges, preventing particle shedding, and maintaining their magnetic properties. Wu et al.[62] synthesized a magnetic, durable, and superhydrophobic PU sponge by binding Fe_3O_4 nanoparticles onto a sponge through a chemical vapor deposition of tetraethoxysilane and then immersing it in a fluoropolymer aqueous solution. The PU sponge became magnetic with a saturation magnetization of 22.73 emu/g after incorporation of the Fe_3O_4 nanoparticles (62.21 emu/g). The prepared PU sponge exhibited very high efficiency in oil—water separation and can rapidly absorb oil slicks from the water surface and heavy oil underwater under the influence of a magnet. In addition, the PU sponge can serve as a membrane for oil—water separation and continuous separation of numerous oil pollutants from the water surface using a pump. The sponge can maintain superhydrophobicity even when stretched to 200% strain or compressed at 50% strain, demonstrating good mechanical properties.[62] In another study, a magnetic hydrophobic composite PU sponge for oil—water separation was prepared by dispersing expanded GE, stearic acid, and Fe_3O_4 magnetic nanoparticles on the backbone surface of a PU sponge.[63] The addition of Fe_3O_4 magnetic nanoparticles endowed the PU sponge with magnetic responsivity, and the composite PU sponge still had a strong oil adsorption capacity after several adsorbing-squeezing cycles.

Tran and Lee[64] transformed a PU sponge from hydrophilic to hydrophobic by coating it with zinc oxide and then enhanced the surface of the PU sponge from hydrophobic to superhydrophobic using stearic acid. Finally, Fe_3O_4 nanoparticles were loaded onto the PU sponge to endow it with magnetic responsiveness for oil spill management. The prepared composite PU sponge featured a water contact angle of 161°, a hexane absorption capacity of (density = 0.66 g/cm^3) of 32.01 g/g, and a diesel oil absorption capacity of 80.98 g/g (density = 0.87 g/cm^3). In this oil—water separation experiment, the oil solution was absorbed and permeated into the sponge, while the water layer remained above the sponge, resulting in a complete separation of the oil and water. The PU sponge exhibited separation efficiencies of 99.89%, 99.88%, 99.87%, 99.5%, 99.2%, 99.0%, and 98.21% for hexane, toluene, dichloromethane, gasoline, soybean oil, diesel engine oil, and vacuum pump oil, respectively.[63] In addition, Habibi and Pourjavadi[64] prepared a superhydrophobic PU sponge (with a water contact angle of up to 159°) by coating the PU sponge with carbon black (CB), Fe_3O_4 modified by hexagonal boron nitride (h-BN) (h-BN@Fe_3O_4), and acrylic resin. Owing to the chemical and thermal stability of h-BN and CB, the modified sponges remained stable under corrosive conditions (pH = 1—14 and salt solutions) and at various temperatures (−12 °C—105 °C). The modified PU sponge exhibited an oil adsorption capacity in the range of 64—176 g, enabling the separation of a large amount of oil or organic solvents, up to 66,400 times its weight, from oil—water mixtures in continuous separation. Furthermore, the modified sponge can be used for oil spill cleanup over 20 cycles without a significant reduction in its adsorption capacity.[64] To solve the issue of rapid and effective separation of highly viscous heavy crude oil from seawater, Habibi and Pourjavadi[65] prepared a PU/polyaniline/h-BN@Fe_3O_4/polyacrylate-oleic acid resin sponge. The prepared sponge exhibited ultralow density, photothermal properties, superhydrophobicity, and high thermal conductivity, with a water contact angle of 158°, a thermal conductivity of 76 W/mK, a density of 0.038 g/cm^3, and a porosity of 97.97%. In addition, as the photomodified sponge was exposed to sunlight, it efficiently converted the light into heat owing to the activity of the photothermal component. Owing to the presence of h-BN, the generated heat was rapidly transferred to the environment to increase the temperature of the high-viscosity crude oil and reduce the oil viscosity, thereby promoting its fluidity and efficient absorption.[66] Recently, a superhydrophobic and superoleophilic NH_2-MIL-101 (Fe)@Fe_3O_4@PDMS@PU sponge was successfully fabricated through a simple method.[67] The water contact angle of modified PU sponge can reach 155.6° and has the ability to flame retardant, which improves its practical application ability. One study used the fine porous properties of cellulose to modify PU foams loaded with Fe_3O_4 nanoparticles.[68] It was found that the modified PU foams maintained a high magnetic responsivity, and still exhibited a significant oil absorption capacity.

In addition to using Fe_3O_4 for PU modification to impart magnetic responsiveness, Wang et al.[69] and Satria and Saleh[70] explored the use of other magnetic nanomaterials, such as iron oxide (Fe_2O_3) nanoparticles and iron stearate nanocomposites. To obtain durable multifunctional superhydrophobic surfaces, Wang et al.[69] reported a method for preparing multifunctional suspensions (c-Fe_2O_3@SiO_2@ polydimethylsiloxane (PDMS) suspensions), named FSP suspensions, in which c-Fe_2O_3 was coated with SiO_2 shells, and PDMS served as the outer layer. The magnetic saturation of the initial c-Fe_2O_3 particles is about 47 emu/g. Due to the magnetic field shielding of the SiO_2 shell, the magnetic saturation of the c-Fe_2O_3@SiO_2 is reduced to 28 emu/g. The introduction of PDMS further reduces the magnetic saturation to 17 emu/g. A superhydrophobic magnetic polyurethane (SMPU) sponge was prepared by immersing the PU sponge in the FSP suspension, which demonstrated excellent oil absorption ability. Since the FSP coating is only attached to the backbone fibers, the pores of the SMPU sponge are partially blocked, which forms the basis for the excellent absorption properties of the SMPU sponge.[69] SMPU can move directionally under the influence of a magnet and absorb oil along a fixed path. In addition, Satria and Saleh[70] used a dip coating method to load PDA/polypyrrole/polyaniline onto PU foam and then incorporated ferric stearate nanocomposites into it via an ultrasonic method to prepare a superhydrophobic/super lipophilic magnetic PU foam. The resulting nanocomposite exhibited a significantly high water contact angle of 164°. After 20 cycles of oil absorption, the water contact angle of the nanocomposite remained stable at 153°, indicating its strong superhydrophobic properties. Recently, there have also been attempts to use functional materials to modify PU to give it magnetic response and improve its oil−water separation efficiency, such as PDA/polypyrrole/polyaniline.[71] In the future, more efficient magnetically responsive PU oil−water separation materials can be further developed.

5. OTHER METHODS FOR MODIFYING PU MATERIALS FOR OIL−WATER SEPARATION

In addition to the aforementioned nanoparticles, natural materials, and magnetic materials for PU modification, alternative strategies are used to modify PU and enhance its oil−water separation efficiency. For example, Huang et al.[72] attempted to prepare porous PU hydrogels with several desirable characteristics such as substrate independence, underwater superlipophobic properties, and good mechanical properties through a simple and effective strategy. In this process, a PU solution was poured into a Petri dish and then stored at 50 °C for 24 h until a dry PU film was formed. Then, the film was removed from the Petri dish and immersed in water until it reached saturation. Porous PU hydrogels were obtained using a self-made mechanical needle array system to generate holes that completely perforated the hydrogels from one side to the other. The prepared porous PU hydrogel exhibited an ultralow underwater−oil adhesion and excellent oil−water separation efficiency (≥99.9%). Moreover, Huang et al.[73] based on the adhesive properties of mussels, used a one-step copolymerization method to prepare a superhydrophobic PU sponge with a multistage structural surface. Particularly, through the copolymerization of dopamine and dodecyl mercaptan in an alkaline aqueous solution, PDA nanopolymers with dodecyl mercaptan motifs were generated on the surface of the PU sponge skeleton. Subsequently, superhydrophobic sponges were prepared with layered surfaces similar to the chemical/topological structure of lotus leaves. Owing to its highly porous structure, superhydrophobic properties, and strong mechanical stability, the sponge exhibited an ideal oil/organic solvent absorption capacity (with a weight increase from 2494% to 8670%). This indicates that the sponge is a promising adsorbent for removing oily contaminants from water.[73]

The preparation of nanofilms with different microstructures via electrospinning technology as oil−water separation materials have a specific application prospect. However, applying these nanofilms in complex and harsh environments remains a significant challenge.[74,75] For example, membrane materials often used in outdoor environments may undergo degradation due to exposure to ultraviolet radiation, leading to a decrease in material properties, including oil−water separation efficiency. In numerous cases, the oil−water mixture contains various corrosive components, such as acids and salts, which can reduce the mechanical properties of the film. For example, there are studies that build a rough microstructure on the surface of the membrane to resist various harsh environments such as strong acids, strong alkalis, and high temperatures, and ensure its oil−water separation effect.[76,77] Therefore, exploring superhydrophobic stretchable nanofiber composites with excellent corrosion resistance and UV resistance is vital. Huo et al.[78] anchored titanium dioxide nanoparticles on thermoplastic PU nanofibers through ultrasound and then obtained superhydrophobic composite membranes after modifying PU/TiO_2 nanofibers with PDMS. TiO_2 nanoparticles significantly enhanced the surface roughness of nanofibers and endowed the material with UV resistance. PDMS can reduce the surface energy of nanoparticles, thereby improving the hydrophobicity of nanofiber films. Huo et al.[78] used a stretchable, fluorine-free superhydrophobic/superlipophilic nanofiber composite film for separating oil−water mixtures, even in the presence of corrosive salts, acids, and bases. The film exhibited high oil−water separation efficiency, throughput, and good recyclability. Furthermore, Wu et al.[79] investigated the PU/GE nanofiber membrane prepared via electrospinning technology for continuous oil−water separation. The membrane exhibited high oil−water separation efficiency and high permeability flux. Recently, Xu and colleagues used a thermally induced phase separation method to composite hydrophobic nanohydrotalcite with PU foam.[80] This modified PU foam can effectively adsorb a variety of organic solvents and has good reusability.

6. CONCLUSION AND PROSPECTS

Various materials modified with PU exhibit good potential applications in oil−water mixture separation owing to their low cost, good mechanical properties, large pore volume, wear resistance, and water resistance. In this paper, methods and mechanisms for modifying PU materials used in oil−water mixture separation are reviewed. These methods mainly include nanoparticle modification, natural material modification, magnetic material modification, and other approaches. The use of these methods can improve the oil−water separation efficiency, mechanical properties, fire resistance, and corrosion resistance of PU materials.

To facilitate the large-scale practical application of PU-based oil−water separation materials, future research should focus on their oil−water separation efficiency and pay more attention to the following aspects. First, we should increase the focus on the evaluation of the environmental impact of PU-based oil−water separation materials in practical applications, including temperature and ultraviolet light. To address this issue, developing multifunctional PU-based materials and evaluating their performance using real crude oil or oil−water mixtures will bridge the gap between laboratory results and practical applications. For example, through the selection of PU surface modifications, it is endowed with photocatalytic degradation performance, multiresponse superwettability transition performance, superlubricating performance, self-healing performance, etc. Second, considering that practical oil−water separation generally requires numerous separation materials, future research should focus on the large-scale production efficiency, cost, and repeatability of modified PU materials. At present, most of the preparation methods of superwetting materials developed in the laboratory are not complicated, but there are still many problems in large-scale production and practical application, such as the use in specific environments, process optimization, wear resistance and stability. Third, current research has mainly focused on the surface modification or surface grafting of the PU foam or sponge. However, future research should explore the preparation of PU in different forms, such as PU hydrogels with varying physical and chemical properties. Finally, based on the hydrophobic and lipophilic characteristics of animals and plants in nature, the relationship between micro/nanostructures and their functional properties is analyzed. For example, with the help of vapor-assisted deposition, the research group deposited carbon networks nanolayers in situ on carbon fiber networks with micron-sized pores to prepare high-efficiency oil−water separation materials.[81] This analysis provides a theoretical reference for further improvements in developing efficient PU-based oil−water separation materials.

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Notes

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