

Research Article

Polyethylene and Polyvinyl Chloride-Blended Polystyrene Nanofibrous Sorbents and Their Application in the Removal of Various Oil Spills

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Polymers provide a wide range of properties, and these properties can be greatly enhanced and modified through polymer blending. Polymer blending combines the properties and advantages of their original polymers. This paper showcases hydrophobic polymers prepared through polymer blending; these blends are characterized and evaluated for their efficiency in the removal of crude oil spills from aqueous media. The application of these blends holds a great deal of importance in preserving the environment and the recovery of lost oil in spills. The blends are produced using polystyrene (PS) as the matrix polymer and individually blending poly(vinyl chloride) (PVC) and polyethylene (PE) with the PS consisting of proportions of 5–20 wt.% each. The blends are then electrospun into bead-free microfibers with interconnected porosities as shown by their respective scanned electron micrographs. All fibrous sorbents showed a high affinity towards the removal of crude oil, motor oil, and diesel spills. The highly viscous motor spill showed a different pattern of sorption onto fibers than that of crude oil and diesel spills. Upon comparing all the studied electrospun fibers to commercially available polypropylene fibrous sorbents, results show that the sorption efficiency of the electrospun fibers is superior. Most notably, both PS-PE5 and PS-PVC5 fibers showed to be highly more effective than commercially available polypropylene (PP) sorbents towards all types of oil spills.

1. Introduction

Polymers are characterized by the ease of fabrication, modification, and functionalization as compared with other classes of materials. It has been also mixed with other classes of materials to make composites that provide the combined advantages of the components of these composites for a wide range of applications [1, 2]. Structural modifications of polymers extend these applications and overcome any possible shortcomings a single polymer may have. Modifications are most often made in the structure and molecular weight of the polymer as well as through using copolymers that will provide joint properties of the copolymer constituents.

An additional method of polymer modification is through blending; a procedure that involves the mixing of

the main polymer in interest with other components to provide a composite mixture or a blend is used, with improved properties [3]. Blending of polymers is becoming increasingly important in different applications to enhance properties, improve processing, or decrease the cost of production [4]. Blending may also involve the addition of a different class of materials to polymers, such as the process of fabricating of clay-polymer nanocomposites [5–7]. Polymer blending is also achieved through the mixing of two or more different polymers in the liquid phase [8]. Mixing polymers of different classes may result in miscible and immiscible blends due to the phase separation phenomenon [9]. Polymer blend miscibility is assessed by viscometry, which also provides information about the interactions of the polymers with each other through blending [10, 11].

Variations in the viscosity of polymer blends affect their processing and properties of the products fabricated thereafter [11]. An example is shown in the use of fiber manufacturing techniques that depend on drawing fibers from their melts or solutions [12–17]. The common feature among these methods is the formation of fibers from viscous polymeric solution or melt under the effect of centrifugal forces or applied voltage. However, these methods produce fibers with dimensions in the micrometer scale, which are therefore characterized by a low surface area. On the other hand, electrospinning is advantageous in the field of fibers fabrication due to its versatility, technical simplicity, and ease of adaptability [18]. Electrospun fibers can be made from solutions or melts of polymers which are then forced through a syringe pump under the effect of high voltage that upon reaching a critical value, overcomes the surface tension of the liquid and then forming a jet of fibers [19]. The production of nano/micro fibers done by the electrospinning process is influenced by both the electrostatic forces and viscoelastic behavior of the polymer [18]. Process parameters, such as solution feed rate, applied voltage, nozzle-collector distance, and spinning environment as well as material properties such as solution concentration, viscosity, surface tension, conductivity, and solvent vapor pressure, influence the structure and properties of electrospun nanofibers [20]. Significant work has been done to correlate the fibers' characteristics to process parameters and to characterize the properties of fibers as a function of process and material parameters [19]. In terms of material property effect, solution concentration has been shown to limit boundaries for the formation of electrospun fibers due to variations in the viscosity and surface tension of polymers and blends [19]. Low-strength solution forms droplets due to the influence of surface tension while higher concentration prohibits fiber formation due to higher viscosity [20]. In addition, electrospun fiber properties, such as fiber diameters and surface morphology produced from electrospinning of poly(ϵ -caprolactone) (PCL), along with blends of PCL with poly(lactic acid) (PLA), were shown to be related to the viscosity and conductivity of the solvents and the blending ratios of cosolvents [21]. Moreover, it was also realized that increasing the PCL amount in blends increased the solution's viscosity, which led to the production of electrospun fibers with larger diameters [21].

One of the environmental applications of fibers made from polymers and blends is in the cleanup of spilled oil and its separation from aqueous media [22]. Fibrous sorbents of natural [23–33] and synthetic [34–38] origins were investigated in this regard; however, their sorption capacity ranges were limited. Electrospun fibers of polystyrene at the $\mu\text{m}/\text{nm}$ scale, as a potential hydrophobic synthetic polymer for oil sorption applications, have been extensively studied [39–41]. The potential of nanoporous PS microfibers for the cleanup of motor, bean, and sunflower seed oils was studied. However, the maximum sorption capacities of these oils were in the range of 20–110 g/g, which were claimed to be 3–4 times higher than those of commercialized polypropylene fibers [40]. Our previous results showed a higher affinity of PS microfibrillar sorbents towards various types of crude oil

spills, approaching 217 g/g [41]. Our experiments showed the dependence of the oil sorption on the crude oil physical characteristics, such as density and viscosity, as well as the properties of the fibrous sorbents and the interconnectivity of their porosity [41].

In addition to the application of fibrous sorbents made of homopolymers, blends, and mixtures of various polymers were also investigated as potential oil spill sorbents [42, 43]. Promising results have been shown for blending PS with PVC [44]. The usage of PS concentrations as a second polymer in PVC dope solution increased the chemical and physical properties of the polymer [44]. According to our recent research, the electrospinning of PS and PVC increased the sorption capabilities of the polymer due to the enhancement of the elastic properties of pure PVC [44]. Similar findings were obtained when PS was blended with PU [45]. In a recent study, polyvinyl chloride (PVC)/polystyrene (PS) electrospun fiber sorption capacities were evaluated for their efficiency in absorbing motor oil, peanut oil, diesel, and ethylene glycol. Results showed higher sorption capacities than commercial polypropylene (PP) sorbents with excellent oil/water selectivity [45].

Through the process of blending, it is assumed that polymer-polymer interactions dominate polymer-solvent interactions. In the case of attraction between the polymers, the two component molecules of macromolecular coils may swell, thus increasing the viscosity due to the increase in the hydrodynamic volume [10]. On the other hand, if repulsion occurs, shrinkage of the macromolecular coils may occur, which leads into a decrease of the viscosity due to the decrease in the hydrodynamic volume [10]. The effect of interfacial tension, viscosity ratios, and solubility on nanofibers with PB/PC, PMMA/PC, and PS/PC blends was evaluated, where it was concluded that the solubility differences of the polymer components in the electrospinning solvent played a key role in the resulting phase structure of the nanofibers [46]. Larger solubility differences led to the formation of core-sheath structures, whereas smaller solubility differences of the components of the blends led to the formation of cocontinuous structures.

The present work investigated the effect of blending low-density polyethylene (PE) and poly(vinyl chloride) (PVC) with a matrix of polystyrene (PS) on the characteristics of the fibrous sorbents prepared, thereafter using an electrospinning technique. The optimally prepared sorbents from PS-PE and PS-PVC blends were further evaluated for their affinity towards the removal of crude oil, motor oil, and diesel spills from simulated sea water media. The results were correlated and compared with those of commercially available fibrous boom. The objective of these experiments is to compare the sorption efficiency of polymer blends with that of neat polymers, as well as comparing the highest sorption capacity blend formulations with the sorption characteristics of a commercially available fibrous sorbent product. This is part of our ongoing efforts to produce high surface area fibrous sorbents with a higher efficiency of oil sorption than commercially available products.

2. Materials and Methods

Polystyrene (PS, $M_w = 350,000$ by GPC), poly(vinyl chloride) (PVC, $M_w = 4,800$ by GPC), and polyethylene (PE, $M_w = 4,000$ by GPC) were purchased from Sigma-Aldrich, USA. N,N-dimethylformamide (DMF), 99.8%, was also purchased from Sigma-Aldrich, USA. Crude oil was obtained TOTAL, Abu Dhabi, UAE. Viscosity of the as-received crude oil was measured as 7.0 cP. A used motor oil, with a viscosity of 244.4 cP, and diesel, with a viscosity of 5.8 cP, were both obtained from a UAE local gas station and were also evaluated for their sorption capacities onto the investigated fibrous sorbents. Viscosity measurements were carried out using a Brookfield viscometer, USA at a 50 rpm.

Blends of PVC and PE with PS containing 5, 10, and 20 wt.% of each of the polymers in PS were prepared by mixing the corresponding amount of each of the polymers with PS in DMF for 24 hours until a completely homogeneous solution is obtained. Viscosity of the obtained PS-PE and PS-PVC blends was measured as a function of the concentration of PVC and PE using a Brookfield viscometer (LV DV-II + Pro EXTRA) by Spindle-S34 at 50 and 100 rpm.

Blends of PS-PE and PS-PVC were electrospun into microfibrillar sorbents using an electrospinning setup (Spraybase, Ireland). A constant volume of 10 ml of each of the blends in a plastic syringe (MicroTouch Syringe, USA) connected to a metal 18 G needle emitter was electrospun into fibers at a constant voltage of 25 kV and a fixed flow rate of 10 mL/h, which were set by the Syringe Pump Pro software. The distance between the emitter and the metallic collector was kept constant at 15 cm. The electrospinning process was carried out in a nonhumid atmosphere at room temperature. Electrospun fibers were collected on an aluminum foil sheet and were left till complete dryness before studying their structural and morphologic characteristics. In contrast, fibrous sorbents made of the pure PS polymer were fabricated using the same set of electrospinning conditions. Additionally, electrospinning of pure PE and PVC polymers was attempted.

Evaluation of the composition of the electrospun fibrous sorbents was carried out using a Fourier transform infrared (FT-IR) spectrometer (IRPrestige-21, SHIMADZU) in a transmission mode and a thermogravimetric analyzer, SHIMADZU (TGA-50). All samples were heated from 0 to 600°C with the heating rate of 10°C/min. Fibrous sorbents were also characterized for their BET surface area, porosity, and pore size distribution were carried out using a N_2 -adsorption instrument (TriStar II PLUS, Micrometrics, USA). The morphology of the fibrous sorbents was evaluated using a scanning electron microscope (SEM) after gold coating. Contact angle measurements of all fibrous sorbents were measured by a water contact-angle system (DM-301, Kyowa Interface Science Co) at 25°C.

Fibrous sorbents obtained by electrospinning at various preparation conditions were evaluated for their performance in the sorption of total crude oil spills from simulated sea water media, following an established ASTM F726 procedure [47]. As in a conventional sorption experiment, a 10 ml

of crude oil was poured into a beaker containing 100 mL artificial seawater (35% NaCl). Based on our previous findings, a constant weight of each of the sorbent, 0.1 g, was then evenly placed onto the oil surface and was left to float freely. After various contact time intervals up to 15 minutes, the oil-containing sorbents were removed, left to drip for 30 seconds and weighed to assess their uptake capacities (in g/g) using the following equation [48]. In order to achieve the equilibrium of uptake, the contact time was further extended to 30 minutes:

$$Q = \frac{m_o - m_s}{m_s}, \quad (1)$$

where Q is the oil uptake capacity (g/g), m_o is the total mass of sorbents after the oil drained, and m_s is the mass of the dry sorbent. The results are expressed as an average of triplicate readings.

3. Results and Discussions

3.1. Viscosity Measurements. Completely homogeneous PS solution in DMF containing 20 wt.% of PS shows a viscosity of 175 cP as measured at room temperature. Upon the addition of 5, 10, and 20 wt.% PVC and PE to PS at room temperature, a remarkable change in the viscosity of the resultant blended mixtures was exhibited, as shown in Figure 1(a). A linear increase in the viscosity of the PVC-PS blends was observed with the increase in the proportion of PVC in the blend, reaching a viscosity of 550 cP with the addition of 20 wt.% of PVC. The effect of adding PE to the PS solution on the viscosity of the produced blends was less pronounced. These findings were supported by the variation in the shear stress of the resultant blends. In addition, visual observation of both types of blends indicated a higher miscibility of PVC with PS in their solution in DMF, while the less miscibility of PE with PS in their solution in DMF was reflected as solid PE particulates being suspended in solution.

3.2. SEM Measurements. The variation of the viscosity of the blends was further confirmed by investigating the morphology of the fibrous sorbents made from all blends by electrospinning, as shown in Figure 2. A nonbeaded fibrous sorbent with a homogeneous fiber and pore size distributions and an average fiber size of 7 μm was obtained after electrospinning pure PS solutions. Upon the addition of PVC and PE to the initial PS solution, a pronounced increase in the fiber size was obtained, as shown in Figures 2(b)–2(h). Compared with the size of the pure PS fibers, the addition of PE and PVC to PS matrix showed an increase in the fiber diameter towards an average diameter of 10 μm and 15 μm , respectively. This is attributed to the increased viscosity of the PS-PVC and PS-PE blends with the addition of PVC and PE, respectively [42]. Despite the increase in the average fiber size, all fibrous sorbents showed a homogeneous fiber size and pore size distribution with a high degree of interconnectivity of the pores. The addition of PVC and PE also resulted in an increase in the

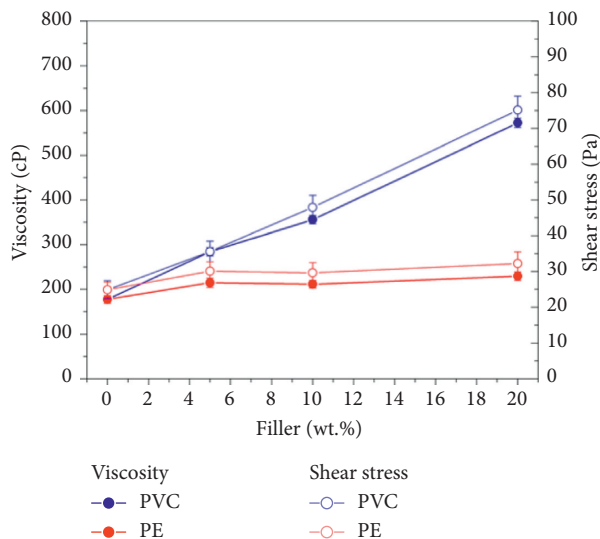


FIGURE 1: Average viscosity and shear stress of PS-PVC and PS-PE blends as a function.

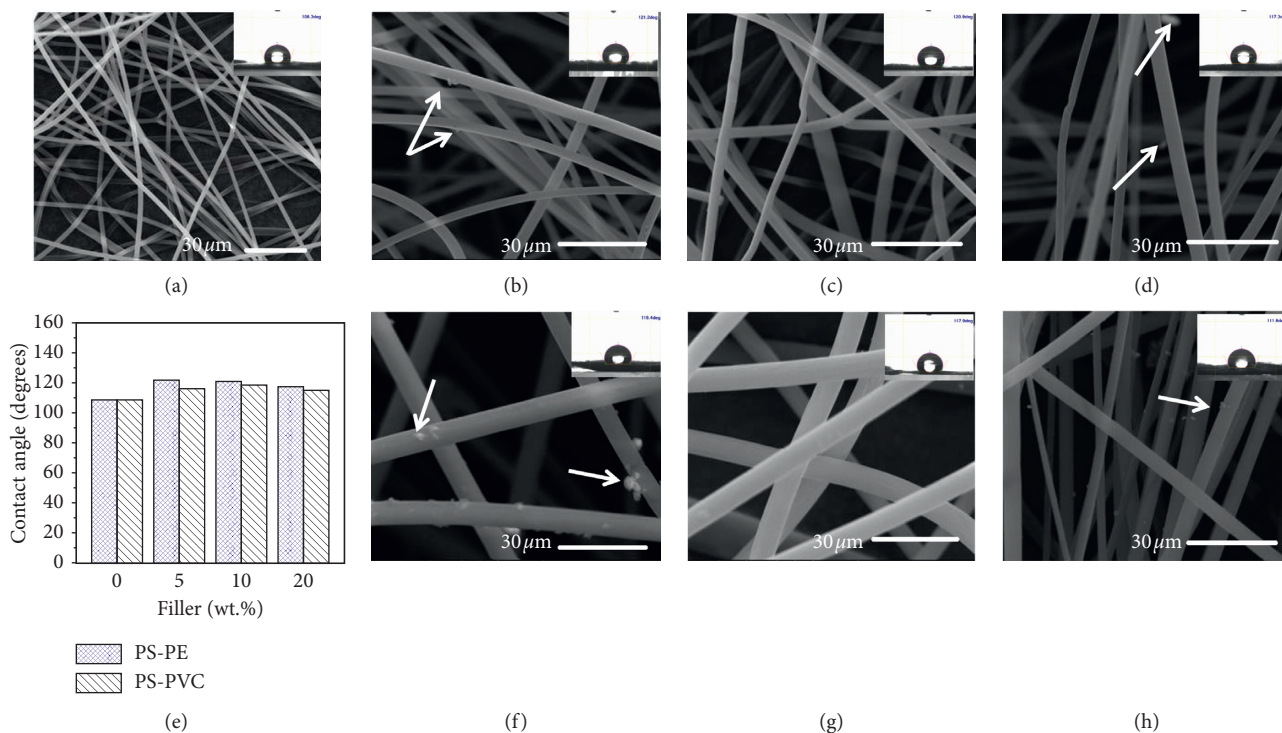


FIGURE 2: Scanning electron micrographs of (a) pure PS, (b–d) PS-PE, and (f–h) PS-PVC fibrous sorbents containing 5 wt.% (b and f), 10 wt.% (c and g), and 20 wt.% (d and h) of each of the additives. (e) Variation of the contact angle with fibers' composition.

hydrophobicity of the fibrous sorbents, as illustrated in Figure 2(e). A pure PS fibrous sorbent showed a contact angle of 108.3° , while PS-PVC blends showed a higher contact angle up to 117.9° . On the other hand, PS-PE blends showed a higher contact angle up to 121° . This could be attributed to the presence of particulates of both hydrophobic polymers (PVC and PE) onto the surfaces of the electrospun fibers, as shown in Figure 2.

3.3. Porosity and Surface Area Measurements. All fibrous sorbents produced from blends of PE or PVC with PS by electrospinning showed a type-IV isotherm with a similar extent of N_2 adsorption, which indicates a similar degree of pore interconnectivity. This was accompanied by a decrease in the BET surface area of the blend fibrous sorbents, as shown in Figure 3(c). A pure PS fibrous sorbent showed a surface area of $52.5 \text{ m}^2/\text{g}$, while a

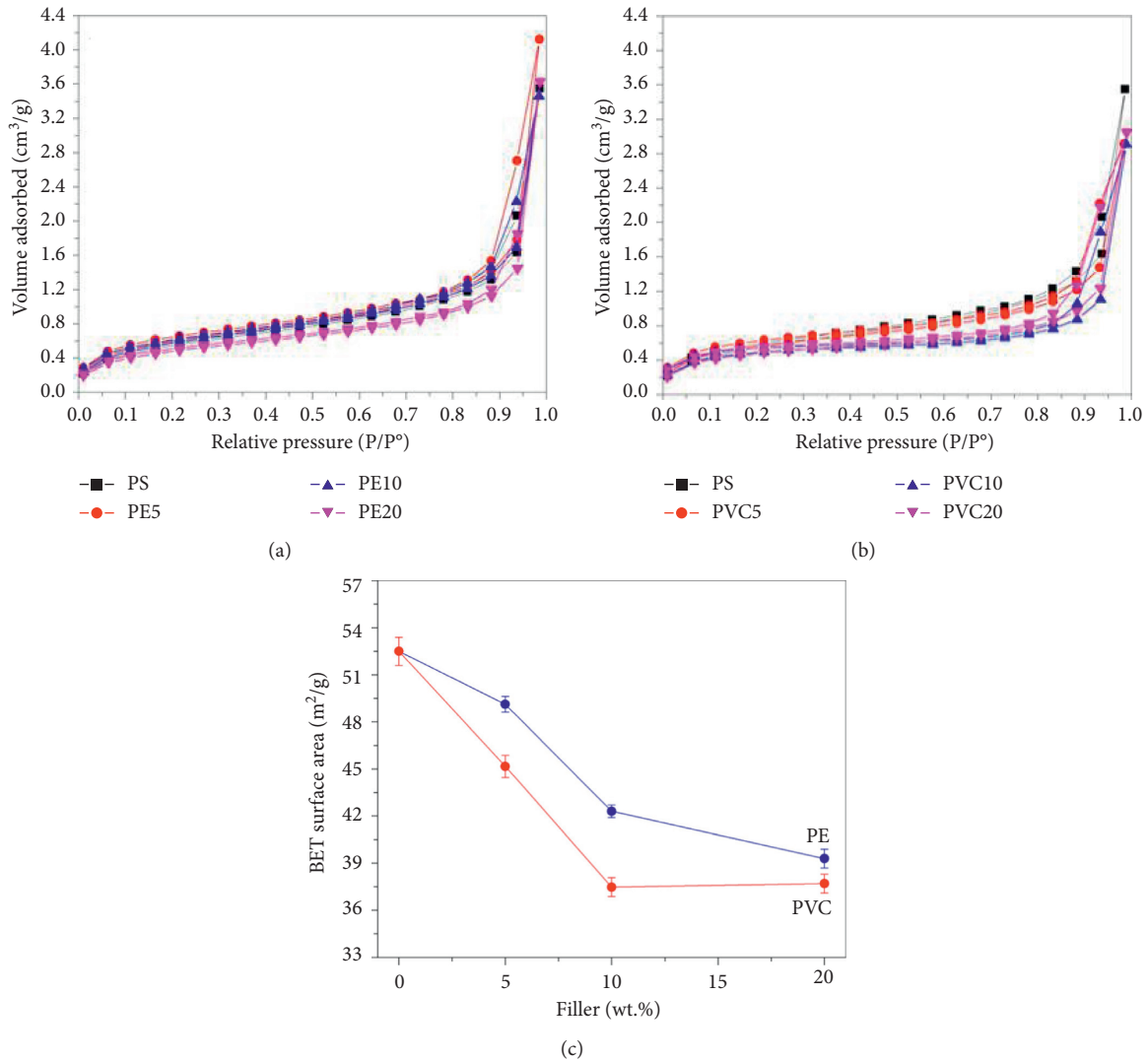


FIGURE 3: N_2 -adsorption isotherms of (a) PS-PE, (b) PS-PVC fibrous sorbents, and (c) their BET surface area.

consistent decrease in the surface area of the PS-PVC and PS-PE blend fibrous sorbent was observed, showing a surface area of 39.5 and 37.5 m^2/g , respectively. A correlation could be also made between the surface area of the PVC-PS fibrous blends and those of the PS-PE fibrous blends with their respective fiber size, where higher surface area of PS-PE fibers was correlated with their smaller fiber size and vice versa.

The presence of each of the additives (PVC and PE) in the fibrous sorbents fabricated from their respective blends with PS was confirmed by FTIR and TGA analyses. FTIR spectra of all fibrous sorbents showed the domination of the spectra with the bands of the PS matrix. The presence of PE and PVC was confirmed by their respective characteristic bands, as explained elsewhere [49, 50]. No extrabands were found, and no major shifts of the bands of the polystyrene matrix were observed. These findings indicate the absence of chemical interaction between each of the fillers and the polystyrene matrix.

3.4. Thermal Analysis. In order to further verify the above findings, fibrous sorbents made from PS-PE and PS-PVC blends were studied by TGA analysis, as shown in Figure 4. The thermogram of pure PS sample shown in Figure 4 indicates a single event of weight loss commencing at 290°C and ending at 420°C and is attributed to the combined degradation and combustion of the polymer. On the other hand, the thermogram of pure PE shown in Figure 4(a) indicates an earlier weight loss starting at 250°C over two steep events with a slow rate of weight loss around 350°C in the middle of the two main events. This was followed by a plateau with a slower weight loss around 475°C until the end of the process. Taken together, these weight loss events denote the degradation and decomposition of the PE polymeric chains leaving behind a carbonaceous residue amounting for the remaining 5% of the starting pure PE sample. On the other hand, the TGA thermogram of pure PVC shown in Figure 4(b) describes a typical behavior of the polymer where it passed through three events of weight loss with different extents until it is completely decomposed [51].

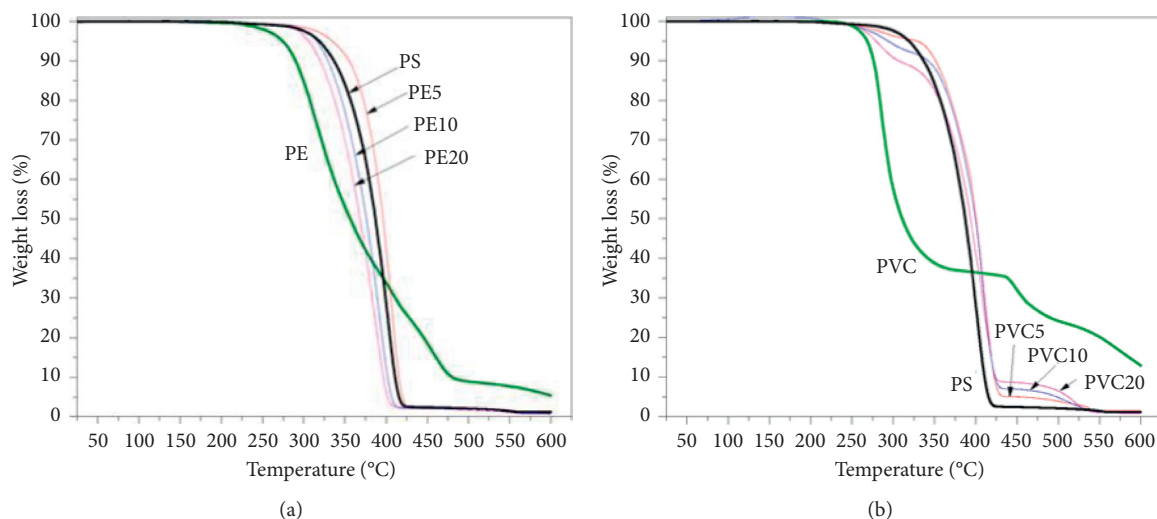


FIGURE 4: Thermogravimetric analysis of (a) PS-PE and (b) PS-PVC fibrous sorbents.

The first event started at 275°C and resulted in a 65% weight loss of the polymer, which is attributed to the loss of HCl from the polymer backbone [51]. This was followed by a second event at 450°C and is comparatively shorter than the first event where a total of 16% of weight loss was shown. This is attributed to the thermal degradation of the polyene backbone, resulting in the formation of volatile aromatic compounds and a stable carbonaceous residue [52]. The residual material underwent a final weight loss of 20% until its complete combustion.

In the presence of various proportions of PE in the PS-PE blends, an overall single steep weight loss event was shown with slight variations depending on the proportion of PE in the original blend, as shown in Figure 4(a). Moreover, all blend fibrous sorbents reached the same final plateau at 420°C as a result of the total degradation and decomposition of the polymeric fibers. With the addition of different proportions of PVC, on the other hand, the fibrous sorbents made of its blends with PS showed a delayed weight loss with the same onset of pure PS around 290°C, as shown in Figure 4(b). The removal of HCl from the PVC component of the blend was evident in the blends containing 10 and 20 wt.% of PVC. On the contrary, the decomposition of the remaining polyene of PVC started earlier at 425°C than that of pure PVC. Similarly, complete decomposition, which is shown by the third event, started earlier around 500°C.

3.5. Evaluation of Oil Uptake Capacity. Fibrous sorbents based on blends of PE and PVC with PS were evaluated for their efficiency to collect three type of spills; crude oil, motor oil, and diesel from a simulated sea water medium. Our previous findings showed the high efficiency of sorption of crude oil spills using microfibrillar sorbents that were made from pure polystyrene [41]. These sorption characteristics of pure PS fibrous sorbents were attributed to the high surface area of its microfibrils, high interconnectivity of the sorbent, and high affinity towards crude oil by virtue of its high

hydrophobic characteristics. These characteristics were also maintained in the sorbents made of PS-PE and PS-PVC blends, where a similar pattern of an initial instant sorption of crude oil after 30 seconds of contact between the sorbent fibers and the oil spill was observed as shown in Figures 5(a)–5(e). The highest sorption capacity of a pure PS fibrous sorbent to crude oil spills was found to be 83 g/g within 30 seconds of contact, while all fibrous sorbents made of PS-PE and PS-PVC blends showed higher sorption capacities. The higher hydrophobic PS-PE fibrous blends showed a consistent increase in the uptake capacity of crude oil with the increased content of PE in the fibrous blends, where the highest uptake capacity of 130 g/g was achieved with PS-PE blends containing 20 wt.% PE (Figure 5(a)). On the other hand, the less hydrophobic PS-PVC showed a comparably similar pattern of uptake capacity of crude oil with the highest value of 108 g/g achieved with PS-PVC blends containing 5 wt.% PVC (Figure 5(d)). Upon the instant adsorption of the crude oil onto and into the fibers, a slower resolution stage was observed during the following 2 minutes and ending after 5 minutes of the first contact of the sorbent with oil. During this stage, the oil absorbency of the fibrous sorbents decreased by an average of 10% of its original uptake capacity. The oil contained in the fiber lumen and the interfiber interstices drained out slowly, as the capillary pressure and the van der Waals forces were insufficient to hold the weight of the oil [50, 51]. Moreover, it could be also attributed to the formation of agglomerates between the fibrous sorbents and the first adsorbed layer of crude oil, while the following adsorbed crude oil layers were leaked due to their weak adsorption to the fibers [53]. On a separate experiment, slow addition of crude oil to pure PS fibrous sorbents showed this pattern of initial agglomeration due to the strong adsorption of the oil onto/into the fibers and the eventual solvation of the fibers by the adsorbed oil, as discussed in Figure 6. A sustained lower rate of leaching out of the oil was observed as a plateau for the remaining 25 minutes of all experiments. It should be mentioned that the amounts of desorbed crude oil from all fibrous sorbents

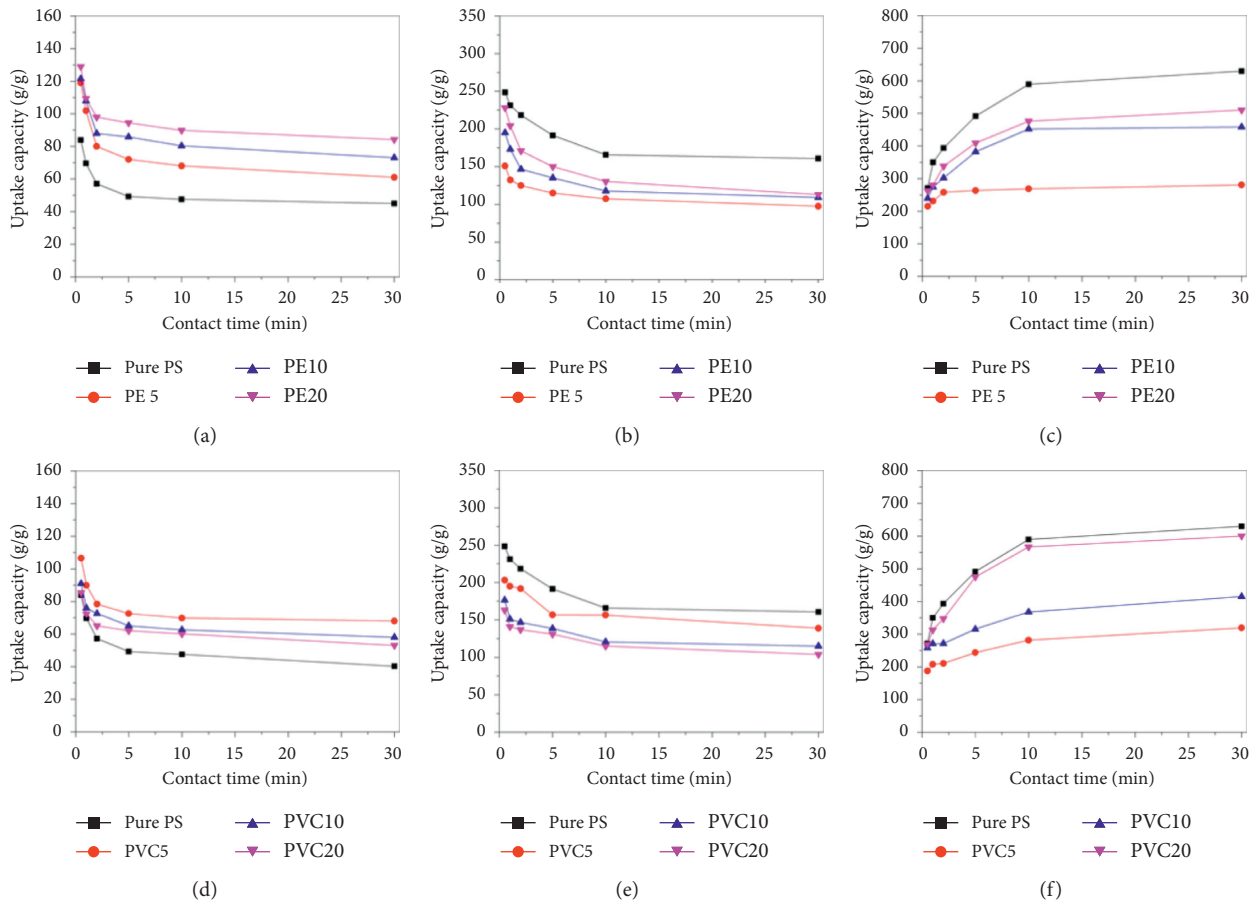


FIGURE 5: Uptake capacity of PS-PE (a–c) and PS-PVC (d–f) fibrous sorbents to crude oil (a and d), diesel (b and e), and motor oil (c and f) spills.

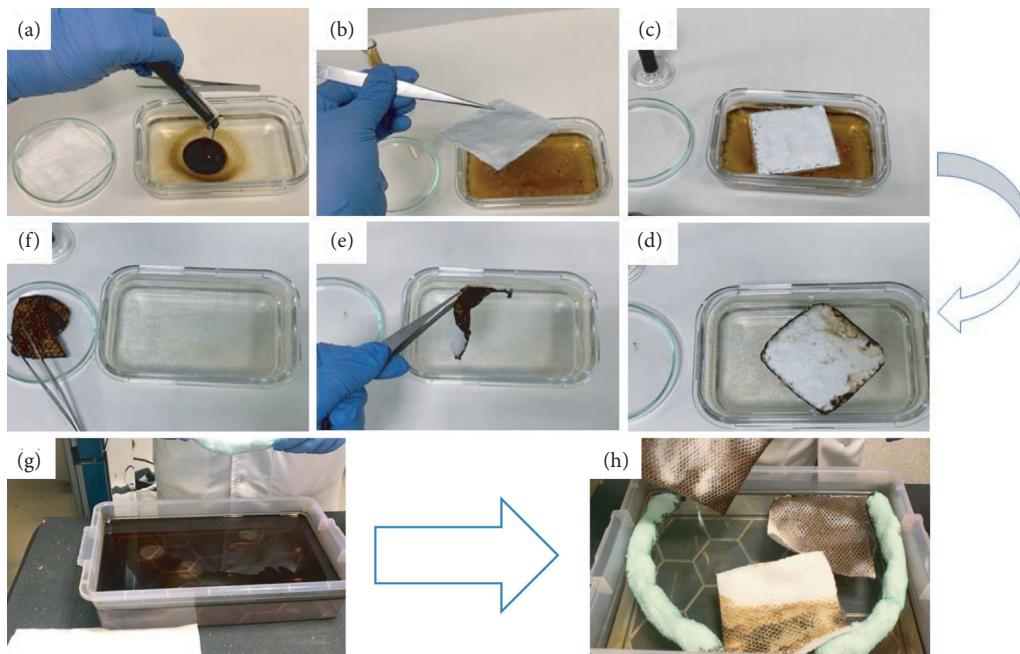


FIGURE 6: Demonstration of oil spill removal using a typical sheet containing PS fibrous sorbents.

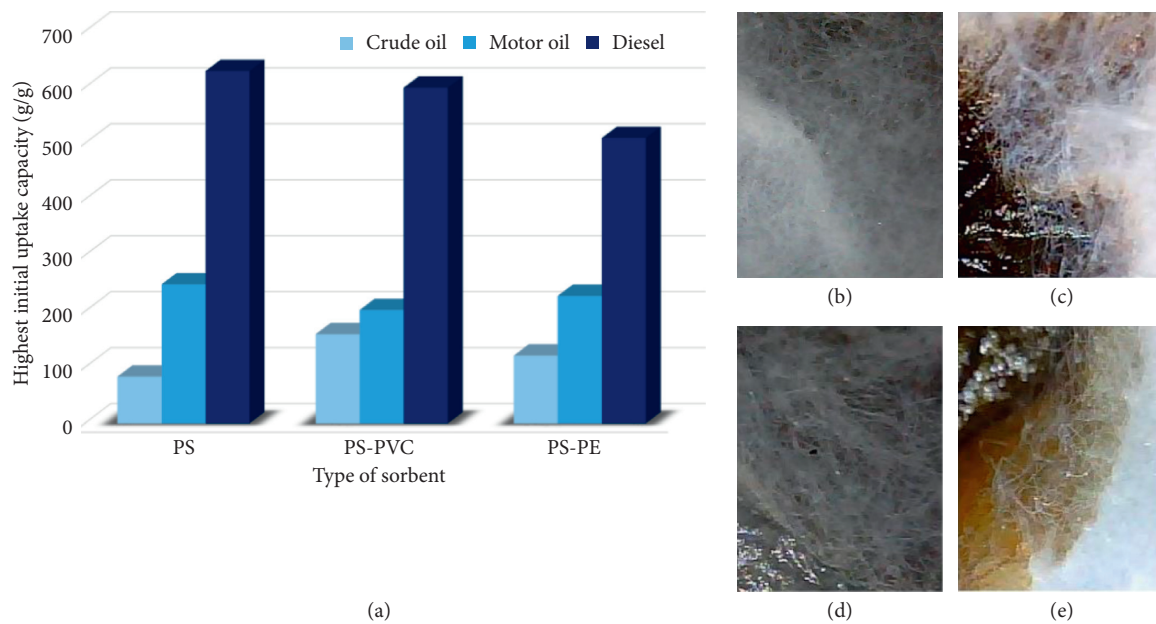


FIGURE 7: (a) Highest uptake capacity of PS-PE and PS-PVC fibrous sorbents to crude oil, motor oil, and diesel spills. Optical images of PS fibrous sorbents (b) as prepared, (c) after crude oil spill sorption, (d) after diesel spill sorption, and (e) after motor oil spill sorption.

during the desorption stages were 40% of their original sorbed oil after 30 seconds.

A similar pattern of sorption was observed when the fibrous sorbents were immersed in diesel spills (Figures 5(b) and 5(e)), where an instant sorption of the diesel spill was observed followed by a sustained decrease of the sorbed diesel due to the segregation of the fibers within the diesel spill and the detachment of the unabsorbed diesel. The affinity of a pure PS fibrous sorbent towards the diesel spill was found to be higher, with an uptake capacity of 250 g/g after 30 seconds of contact.

In the presence of PE and PVC, blend fibrous sorbents showed a lower affinity with sorption capacities of 150–230 g/g and 165–205 g/g, respectively. The lower viscosity of diesel (5.8 cP) compared to that of crude oil (7.0 cP) may explain the higher instant sorption onto all types of fibers and consequently the higher extent of release of the adsorbed diesel. This is attributed to the easier flow of diesel within the fibrous sorbent and the detachment of the weakly adsorbed diesel.

A different sorption profile was observed when pure PS fibrous sorbents and its blends with PE and PVC were used for the removal of the motor oil spill, as shown in Figures 5(c) and 5(f). An instant uptake capacity of 265 g/g of motor oil was achieved using a pure PS fibrous sorbent after 30 seconds of contact between the fibers and the motor oil. This was followed by a continued sorption of the motor oil into and onto the highly porous fibrous sorbent within the following 10 minutes of contact between the fibers and the motor oil. A plateau was reached thereafter where a maximum uptake capacity of 625 g/g was achieved after 30 minutes. In the presence of PE and PVC in the blend fibrous sorbents, a similar pattern was shown with a lower affinity of sorption towards motor oil than that of a pure PS fibrous

sorbent. The overall different profile of sorption of all fibrous sorbents to motor oil is, therefore, attributed to the higher viscosity of motor oil (244.0 cP) as compared with that of crude oil (7.0 cP) and diesel (5.8 cP). The highly viscous motor oil, therefore, slowly flows and diffuses onto and into the pores of the fibrous sorbents, which explains its increased sorption pattern on all fibrous sorbents within the first 10 minutes and right before reaching the plateau.

Figure 7(a) summarizes the highest uptake capacities of all fibrous sorbents to the three types of spills after 30 seconds of contact. Despite the higher affinity of a pure PS fibrous sorbent to motor oil than that of PS-PVC and PS-PE blends, they showed a higher affinity towards crude oil and a comparable affinity towards diesel. It should be mentioned, however, that the obtained uptake capacities of all sorbents to the investigated oil spills are higher than those reported in the literature [43]. This is highly attributed to the enhanced affinity of the high surface area fibrous sorbents and the interconnectivity of their porosity, as shown in the optical images of the sorbed spills (Figures 7(c)–7(e)) onto a pure PS fibrous sorbent, as compared with that of the as-prepared PS fibrous sorbent (Figure 7(b)). The integration of the oil spills onto and within the fibrous sorbent takes place through a capillary phenomenon, which is dependent on the high surface area and interlocking of the sorbent fibers as well as the interconnectivity of the inherent porosity of the sorbent [54]. In addition to these sorbents inherent characteristics, the hydrophobicity of the sorbent fibers has been proven to enhance their compatibility with the highly hydrophobic oils. The sorption of a crude oil spill is demonstrated in Figure 6 using a typical fibrous sheet. The high cleaning efficiency of the fibrous sorbent via the collection of the spilled crude oil is evident in Figure 6(d). On the other hand, Figures 6(e)–6(f) show the clot formed by the fibrous

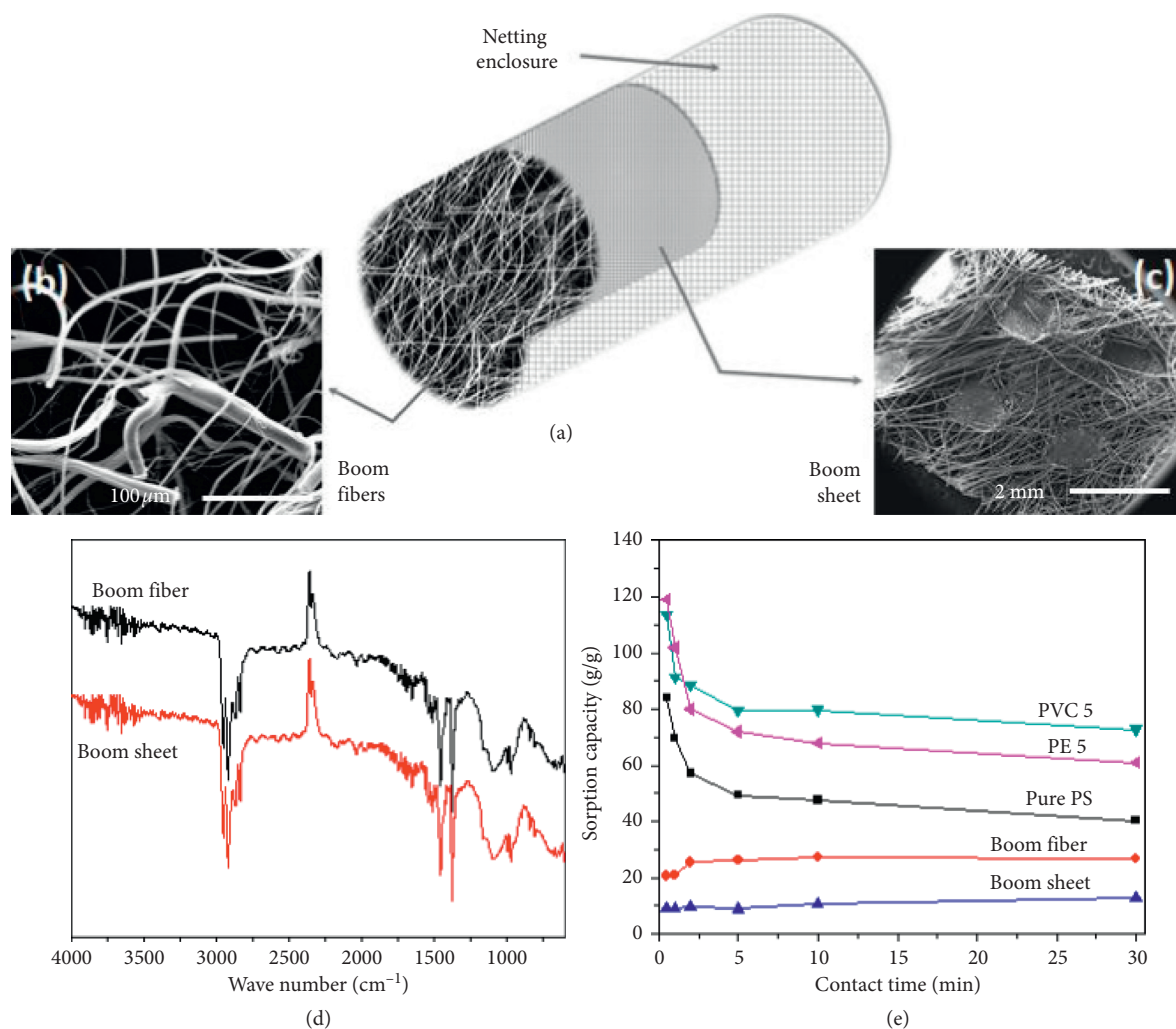


FIGURE 8: (a) A schematic structure of a typical fibrous boom. SEM micrographs of the internal boom fibers (b) and the boom sheet (c), (d) infrared spectra of the commercial boom fibrous sorbent and its sheet, and (e) uptake capacity of a commercially available polypropylene boom fibrous sorbent and its sheet as compared with that of pure polystyrene and blends of polystyrene with 5 wt.% of each of PE and PVS.

sorbent and sorbed crude oil, which was then collected leaving behind oil-free water.

In contrast, a commercially available polypropylene (PP)-based fibrous boom was investigated for its structure, morphology, and uptake capacity of the crude oil spill. Figure 8(a) shows a schematic structure of a typical fibrous boom, where the main sorbent material is in the bulk of the boom, surrounded by a thin low-lint sleeve that keeps the fibers intact. An external highly porous netting sleeve makes the overall final shape of the boom and helps in the handling of the boom. Figures 8(b) and 8(c) show the microstructure of the boom fibrous adsorbent material (b) and the boom external sheet (c). The sorbent material is made of a non-woven fibrous assembly that was fabricated by melt-blowing polypropylene with a heterogeneous fiber size distribution and an average fiber size of 12 μm, which is 10 times higher than the average diameter of the PS, PS-PE, and PS-PVC fibers prepared in the current study. On the other hand, the external boom sheet is also made of a fibrous sheet of thicker fibers that are arranged in square-shaped macropores,

1 mm² area, which are made within the sleeve to facilitate the passage of oil to the fibrous sorbent. Both of the types of fibers used in the fabrication of the fibrous sorbent and the thin sheet are made of polypropylene, as shown in their IR spectra in Figure 8(d).

A typical sorption experiment of a crude oil spill was carried out using the boom fibrous material and the boom external sheet independently to assess their sorption efficiency. Results were compared with that of pure PS and blends containing 5 wt.% of PE and PVC, as shown in Figure 8(e). The pattern of oil sorption of the boom material showed an initial increase in the adsorbed oil until an equilibrium was reached after 2.5 minutes. However, the highest uptake capacities of the boom fibers and thin sheet were 10.5 and 26.5 g/g, respectively. These low oil uptake capacities were attributed to the lower surface area of the polypropylene fibers, despite the high hydrophobic nature of the fibers. It should be noted that both types of boom materials showed retention of the adsorbed oil, where both materials maintained their equilibrium sorption capacities

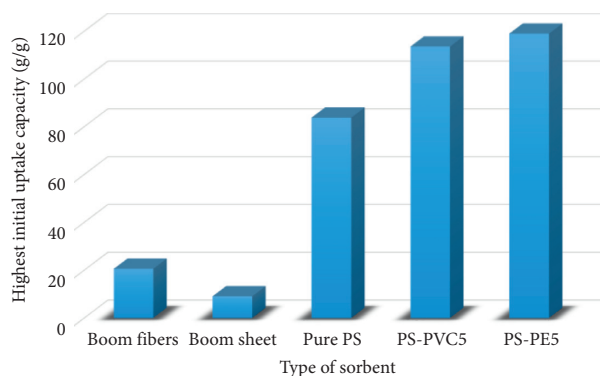


FIGURE 9: Highest uptake capacity of pure PS, PS-PE 5, and PS-PVC 5 fibrous sorbents, as compared to those of a commercially available boom fiber and sheet to crude oil spills.

throughout the duration of the experiment. In contrast, PS-PE5 and PS-PVC5 fibrous sorbents used in the current study showed an instantaneous sorption within the first 30 seconds, followed by the release of the weakly adsorbed oil. Despite the weaker retention of the synthetic fibers, their uptake capacities after 30 minutes were still higher than that of the commercial boom material. Figure 9 compares the highest sorption capacities of the commercial boom fibers and sleeve materials as well as the PS, PS-PVC5, and PS-PE5 fibrous sorbents investigated in the current study. The results shown in Figure 9 confirm the superiority of the proposed PS, PS-PE, and PS-PVC blends as fibrous sorbents for the removal of crude and motor oils as well as diesel, as compared with commercially available boom material.

4. Conclusions

This current study investigated the formation and properties of fibrous sorbents made of PS-PVC and PS-PE blends, as well as their efficiency as sorbents for the removal of crude oil, motor oil, and diesel spills. Blends made of PS as the main polymer and up to 20 wt.% of PE or PVC were electrospun into microfibrillar sorbents with homogeneous fiber size and pore size distributions. Fibrous sorbents showed an increased combined hydrophobicity with the addition of PE and PVC before electrospinning, and were tested accordingly as oil spill sorbents. Results showed the enhancement of sorption kinetics of all types of spills with the presence of PE and PVC in the fibrous sorbents, which was attributed to their role in increasing the hydrophobicity of the blend fibers. Compared with commercially available PP fibrous sorbents, it was found that PS-PVC5 and PS-PE5 sorbents were superior with 112 and 119 g/g oil uptake capacity, respectively. These values are more than 5 times higher than that of PP. These findings recommend their applications as potential sorbents for the cleanup of various oil (crude, diesel, and motor) spills.

Data Availability

All results shown in the manuscript are based on original work performed in our laboratories.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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