Training Engineering Students on Synthesis and Characterization of Superhydrophobic Electrospun Nanocomposite Fibers from Recycled Polystyrene Foams

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Abstract

The scarcity of pure drinking water is one of today's major humanitarian challenges around the globe. The world population growth, urbanization, depleting water resources, deteriorating water quality, and global climate change have intensified this crisis, especially in countries with arid and semi-arid regions. Also, the production of different plastic wastes is increasing day by day and, therefore, a growing concern to the serious environmental challenges. These wastes are rarely dissolved by microorganisms, and hence, the recycling of value-added materials is essential. In this work, recycled expanded polystyrene (REPS) foam with various proportions of titanium dioxide (TiO_2) nano- and aluminum (Al) microparticles was spun into superhydrophobic nanocomposite fibers using the facile electrospinning technique and proposed for harvesting fog from the atmosphere. The fiber morphology and thermal properties as well as surface hydrophobicity of the nanocomposite fibers were investigated. Test results show that the as-prepared nanocomposite fibers exhibit superhydrophobic characteristics with a water contact angle of 152.03°. These electrospun superhydrophobic nanocomposite fibers from REPS have various industrial applications, including water collection, water filtration, tissue engineering, and composites. During the present study, undergraduate and graduate students worked together to learn every steps of the project.

Keywords: Recycled EPS Foam, Fog Harvesting, Water Contact Angle, EPS Nanocomposite Fiber, Electrospinning.

1. Introduction

In recent years, the scarcity of pure drinking water has become one of the main global concerns, especially in countries with arid and semi-arid regions. These areas suffer from unusually low rainfall, and therefore, some of the animals, plants, as well as human beings depend on fog, mist, and humid air for their source of water. Around the world, about one billion people are suffering from lack of fresh drinking water [1]. In some Asian, African, and Latin American countries, unconventional methods such as rain and groundwater harvesting, cloud seeding, and desalination are already being employed to produce pure water for drinking, agriculture, medical, industrial, and other purposes [2]. In addition, some plants, for example *Cotula fallax* in South Africa, have a three-dimensional hierarchical structure and their leaves have a hydrophobic surface, which can collect water from the atmosphere. Also, the Cactaceae family and green bristle grass can effectively capture water from fog [3-4]. In the past decade, extensive research has been done on mimicking nature to develop a cleaner and more efficient way of capturing atmospheric water in managing the issue of pure water scarcity. For efficient fog harvesting, hydrophobicity and hydrophilicity of the collector materials for fast water capturing and easy drainage properties have a significant effect. Moreover, superhydrophobic surfaces have other advantages such as self-cleaning, stain resistance, and drag reduction, and oil spillage separation [5-6].

In 2016, around 335 million metric tons of plastics were produced globally, and only nine percent of waste plastic that was produced ended up being recycled [7]. These large amounts of plastic waste create serious environmental and economic concerns because they are not biodegradable and rarely dissolved by microorganisms. Recycling and reducing the production of plastics have significant industrial importance because doing so reduces greenhouse gases, water and air pollution, and soil contamination, in turn conserving natural resources [8]. Among the various plastics on the market, expanded polystyrene (EPS) foam is commonly used for insulation and packing materials and many other industrial applications. After use, it normally ends up in landfills or is incinerated. Recycling EPS foam into valuable fibers could be a sustainable solution to addressing environmental issues. Such fiber materials are extensively employed in wastewater treatment, energy storage, air purification, selective oil absorption, biological and chemical sensors, tissue engineering, composite reinforcement, and many other applications [9-14].

Sow and Singhal fabricated submicron hydrophobic fibers via a solution blow spinning technique using waste EPS for oil-water separation [15]. They employed a cost-efficient environmental solvent, like ethyl acetate, to dissolve the waste EPS, and they studied the effect of polymer solution properties and operating parameters on the spray morphology. In addition, the fiber spinnability limits were investigated to determine the optimum operational parameters. The fibers mats produced had enhanced hydrophobic and superoleophilic behavior, with a water contact angle of ~138°, oil contact angle of ~0°, and maximum separation efficiency of 97% for free oil (diesel)-water mixtures, thereby providing potential applications in oil recovery and treatment of oily wastewater. Zander et al. synthesized electrospun nanofibers about 100 nm in diameter from bottle-grade polyethylene terephthalate (PET), Styrofoam, and polycarbonate from compact discs (CDs) [16-19]. These nanofibers exhibited good mechanical properties, i.e., elastic moduli ranging from 15 to 60 MPa and stiffnesses similar or greater than fibers made from commercial polymers of equivalent molecular weight. The recycled PET fibers comprised of 1 μm particles had greater than 99% water filtration efficiency and are suitable candidates for ultra/microfiltration, composites, and tissue engineering. Khan and his coworkers fabricated electrospun nanocomposite fiber from recycled polystyrene (PS) [8]. Here, multiwall carbon nanotubes (MWCNTs) and NiZn ferrite (Ni0.6Zn0.4Fe2O4) nanoparticles (NPs) were incorporated into the fiber, and the resulting nanocomposite was studied for its thermal, dielectric, surface hydrophobic, and magnetic properties. The thermal conductivity, dielectric constant, superparamagnetic behavior, and superhydrophobic properties of recycled PS fibers were enhanced by the addition of nanomaterials.

In this work, titanium dioxide (TiO_2) nano- and aluminum (Al) microparticles were encapsulated with recycled expanded polystyrene (REPS), and superhydrophobic nanocomposite fibers were synthesized. The fiber morphology, surface hydrophobicity, and thermal characteristics were investigated. These fibers find applications in air, water, and oil filtration; fog harvesting; advanced composites; thermal insulators; battery and supercapacitor separators; and other infrastructures.

2.0 Experimental

2.1 Materials

EPS was collected from various sources including general shipment packaging, electronics packaging, and laboratory chemicals packaging and then clean, rinsed, and chopped into smaller pieces. Dimethylformamide (DMF) (99.8%) and acetone were purchased from Fisher Scientific. TiO_2 nanopowder with an average particle size of 40 nm (anatase, 99.5%) was purchased from U.S. Research Nanomaterials Inc., Houston, TX, USA. Aluminum microparticles (99.7%, 10 µm) were also purchased from U.S. Research Nanomaterials, Inc., Houston, TX, USA. The purchased TiO_2 and Al nanomaterials used in this study were original without any modifications to the supplier specifications.

2.2 Fabrication of Electrospun REPS Nanocomposite Fibers

The nanocomposite fibers with various weight percentages of TiO_2 nano- and Al microparticles were fabricated by the electrospinning process. The concentration of nanomaterials in the nanocomposite were 0, 5, 10, and 15%. The typical fabrication process was as follows: The waste EPS was chopped into small pieces and dissolved in DMF and acetone at a solvent and polymer weight ratio of 80:20. The mixture was subjected to stirring on a hot plate for 4 hours at a temperature of 40°C in order to obtain a homogeneous blend/dissolution of the polymeric solution. The required amount of TiO_2 nano- and Al microparticles and hydrophobizing agent (1H,1H,2H,2H-Perfluoro-octyltriethoxysilane) were added to the mixture while stirring. A probe sonicator was used to sonicate the mixture for 20 minutes. The prepared solution was then transferred to a 10-ml plastic syringe attached with a needle having an inside diameter of 0.5 mm. A copper electrode with a 0.25-mm diameter was attached to the syringe at one end, while the other end of the electrode was attached to a high DC power supply. Then the electrospinning process was carried out at 25 kV DC with a 1 ml/hr feed rate at a 25-cm distance between the needle and collector screen. The fabricated electrospun nanocomposite fibers were dried on the screen collector for 24 hours at room temperature followed by 5 hours of drying at 60°C in an oven, in order to remove all residual solvent and trapped moisture. The electrospinning process parameters were kept constant for all samples fabricated in this study. Figure 1 shows a schematic diagram of the electrospun nanocomposite fibers fabrication process.

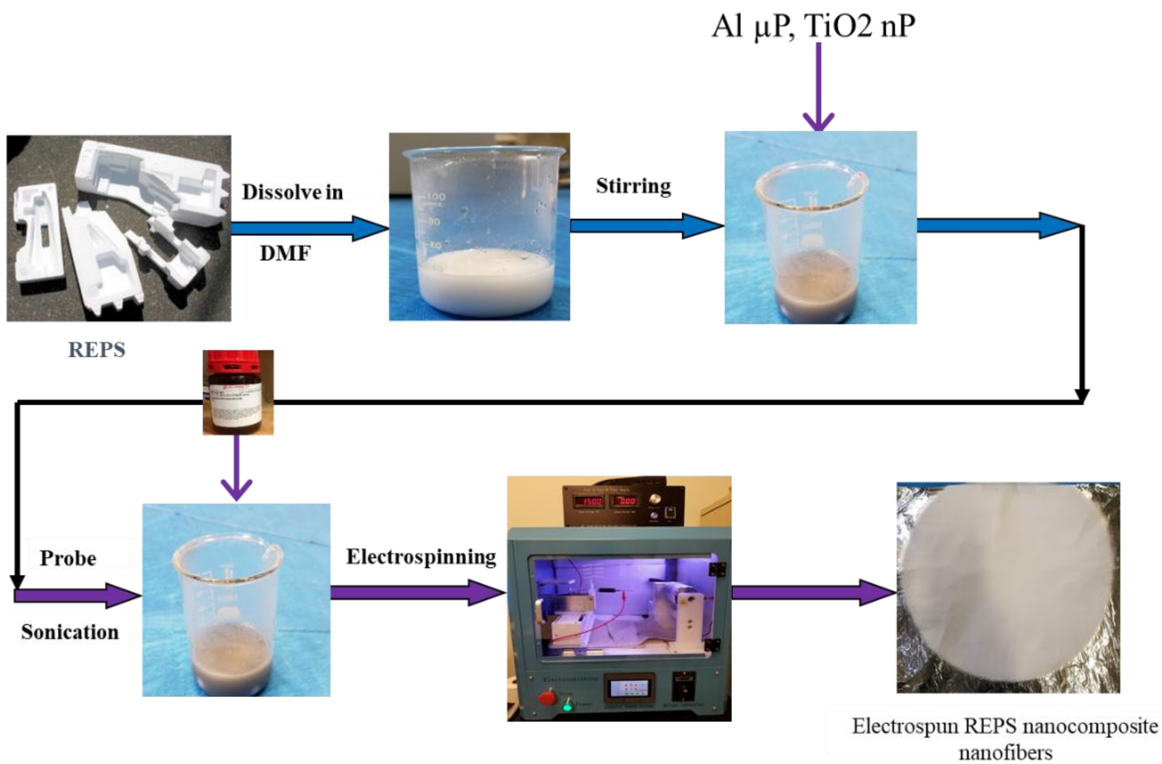

Figure 1. Step by step fabrication process of electrospun nanocomposite fibers.

2.3. Characterization of Nanocomposite Fibers

A scanning electron microscopy (SEM) device (FEI Nova Nano SEM 450) was used to characterize the fiber morphology. With SEM, several areas were imaged to inspect the uniformity of fiber diameters, which were measured by image analysis software (ImageJ v 1.34). The roughness of the fibers was evaluated using a Mitutoyo 178-561-02A Surftest SJ-210 Surface Roughness Tester. The thermal transition of the electrospun EPS nanofibers was measured using a Q1000 differential scanning calorimetry (DSC) device (TA Instruments, New Castle, DE, USA) with a heat/cool program, a heating rate of 10°C/min, and a nitrogen flow rate of 50 ml/min. A Q500 thermogravimetric analyzer (TGA) was used to study the thermal stability of the nanocomposite fiber specimens for the temperature range of 20–600°C. The water contact angle of the EPS fibers was measured with a water contact angle goniometer (KSV Instruments Ltd., Model #CAM 100). Computer software provided by KSV Instruments Ltd. precisely recorded and measured the contact angles, and took pictures of the measured contact angles.

3.0 Results and Discussion

3.1 Characteristics of Nanocomposite Fibers

The roughness of the prepared nanocomposite, including average roughness and root mean square, was measured, and is summarized in Table 1. As shown, the surface roughness of the bare REPS had the lowest roughness and was affected considerably by the embedding concentration of the nanoparticles. The surface roughness was increased by increasing the concentration of the NPs, and a rougher surface was observed for the greater concentration. The surface roughness of a nanofiber strongly affects its hydrophobic characteristics.

Table 1. Roughness statistics for prepared nanocomposite fibers.

Nanocomposite Fibers	Average Roughness (Ra, µm)	Root Mean Square (Rq, µm)
REPS	0.780.03	0.95 ± 0.02
REPS + 5 wt% NP	1.35 ± 0.02	1.66 ± 0.03
REPS + 10 wt% NP	1.81 ± 0.04	1.97 ± 0.02
REPS + 15 wt% NP	2.55 ± 0.05	3.28 ± 0.04

The DSC thermogram of the REPS nanocomposite fibers is presented in Figure 2. The glass transition temperature of REPS generally starts at 100°C [17]. However, the heating curves of REPS and REPS + NPs show large relaxations, so the glass transition temperature cannot be clearly identified. As shown in Figure 2, adding nanoparticles changes the heating and cooling patterns of REPS. In the cooling cycle, REPS releases more energy than the REPS + NP addition. Also, it is difficult to identify crystallization temperature of these materials, which is typically seen for REPS.

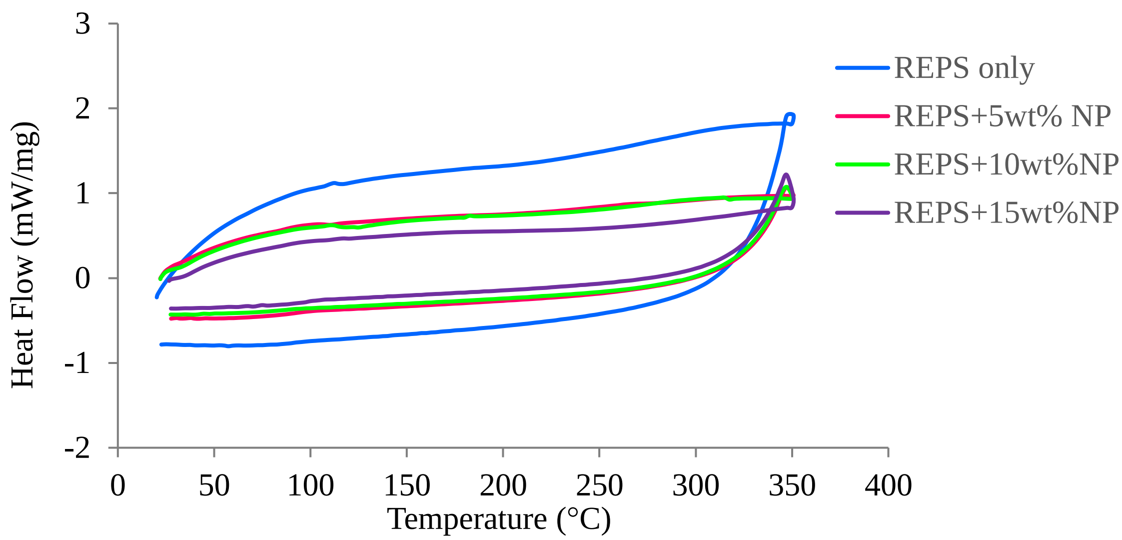

Figure 2. DSC curves for REPS nanocomposite fibers (top curves are cooling runs, and bottom curves are heating runs).

The thermal decomposition of the fabricated fibers was investigated using TGA. Figure 3 shows TGA curves of the REPS fibers and REPS fibers with nanoparticle inclusions. Different mass loss profiles at different temperatures resulted in the inclusion of nanomaterials with REPS. While thermal degradation of the REPS fibers starts around 100°C with a 5% weight loss ($T_{5\%}$) is at a temperature of 386°C, and that of REPS with nanomaterials inclusion is 395°C. This shift reflects that the inclusion of nanomaterials into the REPS improves its thermal stability. Also, char residue at high temperature is much higher with the increasing concentration of nanomaterials for the nanocomposite having nanomaterials into it than REPS fibers only, which also improve the thermal stability.

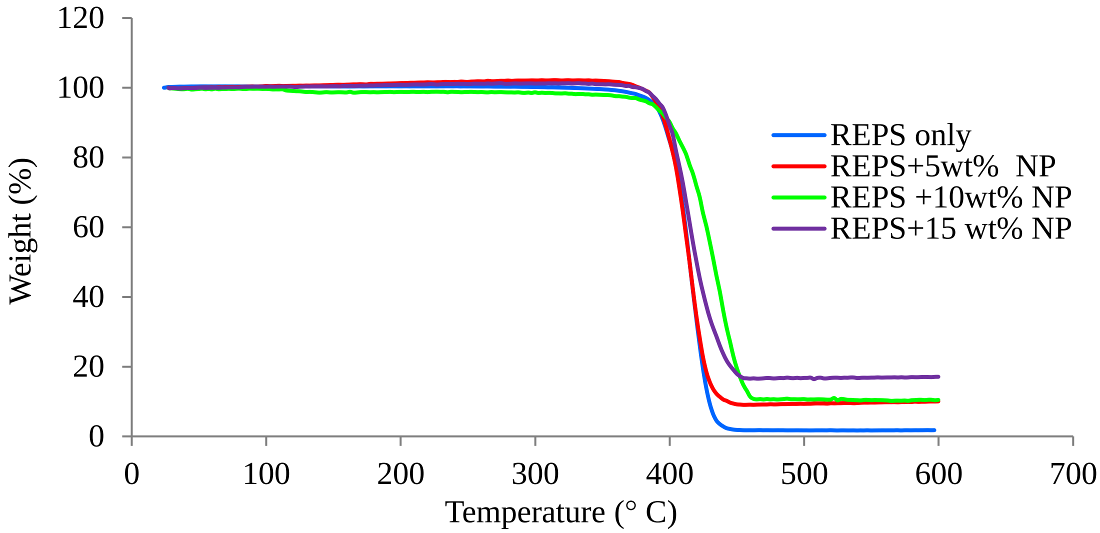

Figure 3. Thermogravimetric curves of REPS electrospun nanocomposite fibers embedded with nanomaterials.

3.2 Fiber Morphology

Nanocomposite fibers were prepared from REPS embedded with different concentrations of nanomaterials via electrospinning to prepare uniform fibers suitable for fog harvesting. Figure 4 displays SEM images of nanocomposite fibers. The REPS fibers without any nanomaterials have uniform diameters and are porous, but the beading was not significant. With the addition of nanomaterials, the beading and agglomeration were significant (5 wt%). However, nanocomposite fibers with 10 wt% nanomaterials have a uniform diameter and rough surface, and beading was not significant. Meanwhile, the addition of 15 wt% nanomaterials produced non-uniform and more agglomerated fibers, fibers exhibited some beads, and there was evidence of fiber breakage. The solution properties such as viscosity, elasticity, conductivity, and surface tension greatly influence the transformation of the polymer solution into nanofibers.

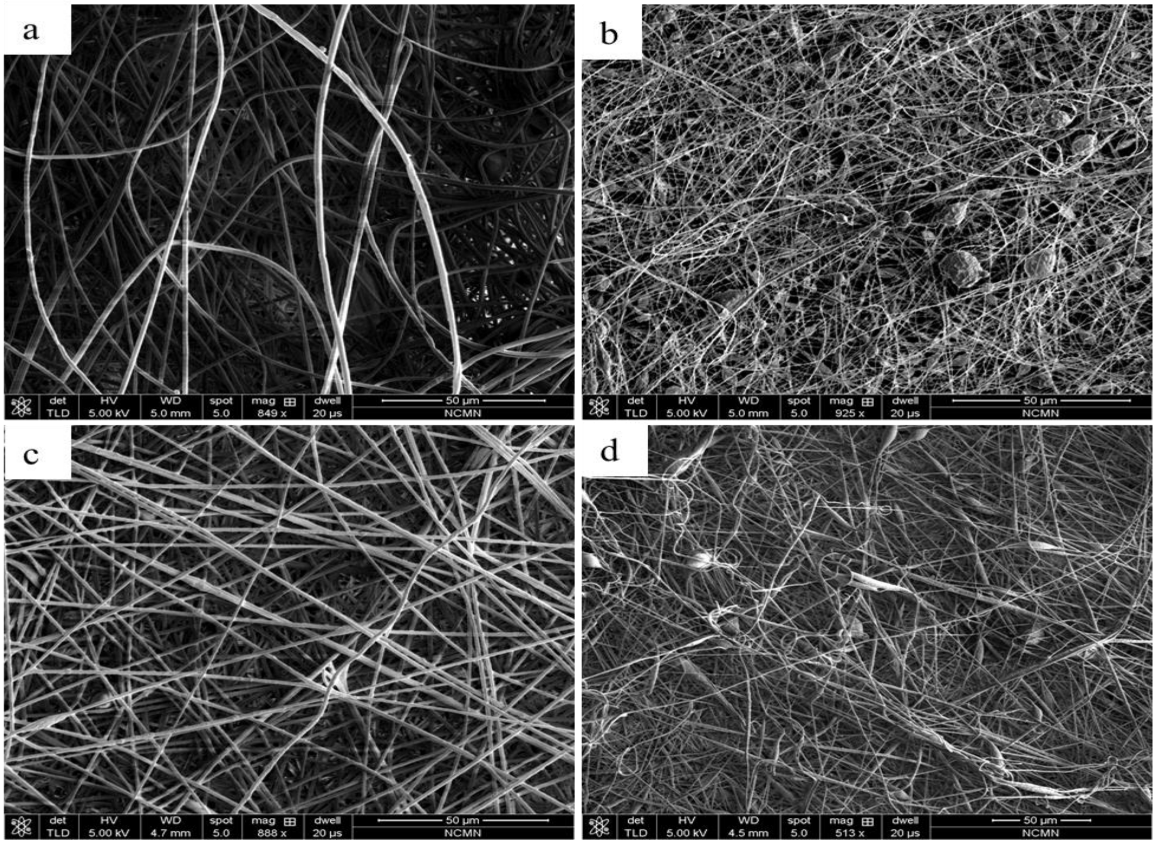

Figure 4. SEM images of electrospun REPS nanocomposite fibers with different concentrations of nanomaterials: (a) REPS only, (b) 5 wt%, (c) 10 wt%, and (d) 15 wt%.

3.3 Hydrophobic Characteristics of Nanocomposite Fibers

Three factors influence the wettability of a solid surface: chemical composition, surface geometrical structure, and homogeneity. The hydrophobic characteristics of fiber surfaces are measured by the water contact angle between the water droplet and the fiber surface. When the water contact angle is greater than 90°, the surface is called hydrophobic. However, with a water contact angle between 150° and 180°, the surface is referred to as superhydrophobic. A superhydrophobic surface exhibits self-cleaning and anti-contamination features [5]. Figure 5 illustrates the water contact angle of REPS nanocomposite fibers embedded with nanoparticles. The REPS nanofibers exhibited an average water contact angle of 116.28°. However, incorporating a combination of micro- and nanomaterials ameliorates the water contact angle to 152.03° (10 wt% nanoparticle inclusion), which is in the superhydrophobic range. Moreover, increasing the nanoparticle inclusion further, such as 15 wt%, reduces the water contact angle. This can be attributed to the fact that the addition of a larger quantity of nanoparticles increases the polymer solution viscosity, agglomeration occurs, and the spin-ability is reduced. Images of the water contact angles of the various REPS nanocomposite fibers are presented in Figure 6.

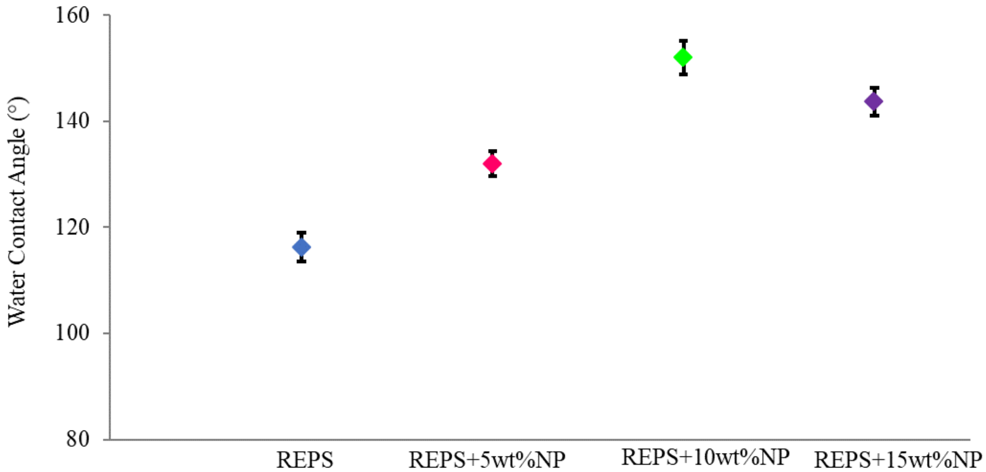

Figure 5. Water contact angle of electrospun nanocomposite fibers.

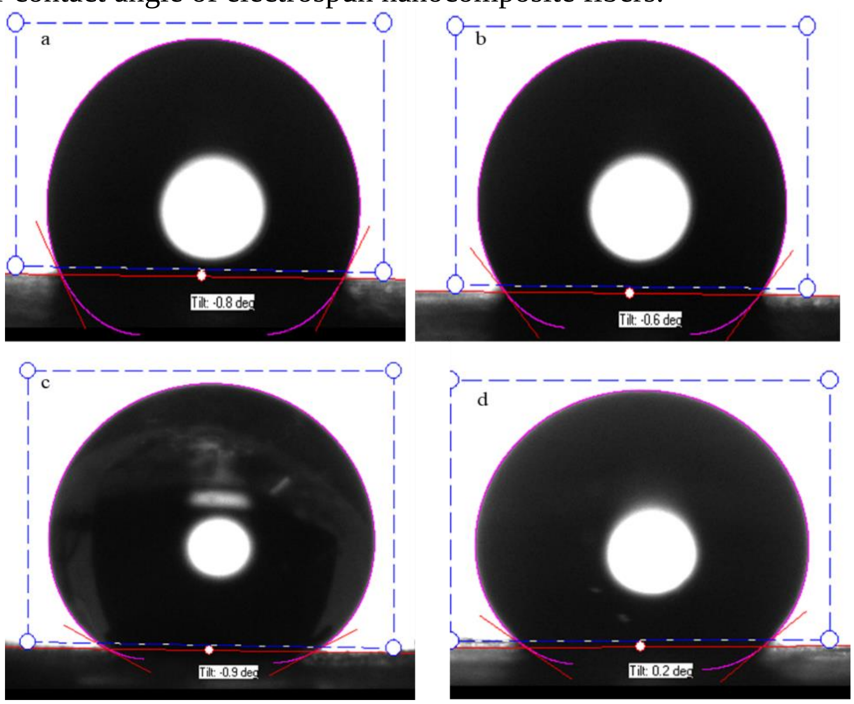

Figure 6. Images of water contact angles of electrospun nanocomposite fibers with various nanoparticle inclusions: (a) REPS only, (b) 5 wt%, (c) 10 wt%, and (d) 15 wt%.

4. Sustainability Training of Engineering Students

Sustainability enables engineers to reduce environmental pollution, cost, and use of natural resources in new designs and products. Due to the limited natural resources and lack of clean water, sustainability should be considered for design and manufacturing. Department of Mechanical Engineering at WSU has over 480 undergraduate and 100 graduate students, and a significant portion of them consider sustainability research projects during their studies. Mr. Polo Osornio-Cornejo (undergraduate student), Mr. Md. Nizam Uddin (PhD Candidate) and Ms. Yeshaswini Baddam (MS student) from the Department of Mechanical Engineering, were involved in the present study, learned many new techniques and gained a lot of new skills and knowledge about sustainability, environmental effects on polymeric structures, their mechanical properties, nanotechnology, and other related technologies and methods. The undergraduate student used these research activities as their study requirements (Engineer 2020) in the College of Engineering at WSU. These students are also co-authors of the present study and made a lot of contributions during the experiments. We believe that sustainability training will enhance the knowledge of many engineering students to perform more detail studies in the future.

5. Conclusions

High-value nanofibers were fabricated from recycled waste polystyrene using the electrospinning method with the addition of nanoparticles and were characterized by SEM, DSC, and TGA. TiO_2 nano- and Al microparticles were included in the electrospun fibers to induce superhydrophobicity on the surfaces of the fibrous films. The effect of incorporation of nano- and microparticles into fibers was investigated. The fibers prepared from only recycled waste polystyrene exhibited hydrophobic properties, with electrospun fiber diameters between 500 nm and 2μm, and an average of approximately 650 nm. However, fibers embedded with 10 wt% nanomaterials showed superhydrophobic characteristics, such as a water contact angle of 152.03°. These experimental results reveal that uniform diameter fibers were produced, and the addition of nanomaterials improved the thermal degradation of the fibers. Meanwhile, a recycling scheme that can address the challenges of polymer recycling has been proposed for waste polystyrene. Overall the prepared nanofibers can be employed for diverse industrial applications, such as fog harvesting, filtration, transportation, energy, defense, and so on. Additionally, undergraduate and graduate students worked in the same project as a team, and learned all the details of the process.

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References

1. K. Onda, J. LoBuglio, and J. Bartram, Global access to safe water: Accounting for water quality and the resulting impact on MDG Progress, Int J Environ Res Public Health, 9, 880-894 (2012).
2. M. N. Uddin, M. Alamir, H. Muppalla, M. M. Rahman and R. Asmatulu, Nanomembranes for Sustainable Fresh Water Production, International Conference on Mechanical, Industrial and Energy Engineering, December 23-24, Khulna, Bangladesh (2018).
3. H. G. Andrews, E.A. Eccles, W.C. E. Schofield, J. P. S Badyal, Three-Dimensional Hierarchical Structures for Fog Harvesting, Langmuir, 27, 3798-3802 (2011).
4. J. Ju, H. Bai, Y. M. Zheng, T. Y. Zhao, R. C. Fang, L. A. Jiang, Multi-structural and multi-functional integrated fog collection system in cactus, Nat Commun, 3, 1247 (2012).
5. A. Khadak, M. N. Uddin, M.M. Rahman, and R. Asmatulu, Enhancing the De-icing Capabilities of Carbon Fiber-reinforced Composite Aircraft via Super-hydrophobic Coatings, The Composites and Advanced Materials Expo (CAMX), October 16-18, Dallas, TX, (2018).
6. M. Salahuddin, M. N. Uddin, G. Hwang, and R. Asmatulu, Super hydrophobic PAN Nanofibers for Gas Diffusion Layers of Proton Exchange Membrane Fuel Cells for Cathodic Water Management, Int J Hydrogen Energy, 43(25), 11530-11538 (2018).
7. Statista, Global plastic production from 1950 to 2017 (in million metric tons), https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/
8. W. S. Khan, R. Asmatulu, S. Davuluri, and V. K. Dandin, Improving the Economic Values of the Recycled Plastics Using Nanotechnology Associated Studies, J Mater Sci Technol, 30(9), 854-859 (2014).

9. H.-J. Kim, S. J. Park, C. S. Park, T.-H. Le, S. Hun Lee, T. H. Ha, H. Kim, J. Kim, C.-S. Lee, H. Yoon, and O. S. Kwon, Surface-modified polymer nanofiber membrane for high-efficiency microdust capturing, Chem. Eng. J. 339, 204–213 (2018).
10. J. Wu, A. K. An, J. Guo, E. J. Lee, M. U. Farid, S. Jeong, CNTs reinforced superhydrophobic-oleophilic electrospun polystyrene oil sorbent for enhanced sorption capacity and reusability, Chem. Eng. J. 314, 526-536 (2017).
11. S. S .A. Kumar, Uddin, Uddin, M. M. Rahman, and R. Asmatulu, Introducing Graphene Thin Films into Carbon Fiber Composite Structures for Lightning Strike Protection, Polym Compos, 40 (S1), E517-E525, (2019).
12. J. Song, H. Wang, Z. Li, Y. Long, Z. Liu, H. Wang, X. Li, M. Fang, B. Li, and H. Wu, Largescale blow spinning of carbon microfiber sponge as efficient and recyclable oil sorbent, Chem Eng J 343, 638–644 (2018).
13. K. Khoshnevisan, H. Maleki, H. Samadian, S. Shahsavari, M. H. Sarrafzadeh, B. Larijani, F. A. Dorkoosh, V. Haghpanah, and M. R. Khorramizadeh, Cellulose acetate electrospun nanofibers for drug delivery systems: Applications and recent advances, Carbohydr Polym 198, 131-141 (2018).
14. D. Morillo Martín, M. Faccini, and M. A. García, D. Amantia, Highly efficient removal of heavy metal ions from polluted water using ion-selective polyacrylonitrile nanofibers, J Environ Chem Eng. 6, 236-245 (2018).
15. P. K. Sow and I. R. Singhal, Sustainable approach to recycle waste polystyrene to high-value submicron fibers using solution blow spinning and application towards oil-water separation, J Environ Chem Eng, (2018). https://doi.org/10.1016/j.jece.2018.11.031
16. N. E. Zander, D. Sweetser, D. P. Cole, and M. Gillan, Formation of Nanofibers from Pure and Mixed Waste Streams Using Electrospinning, Ind. Eng. Chem. Res. 54, 9057-9063, (2015).
17. M. D. Samper, D. Garcia-Sanoguera, F. Parres, and J. Lopez, Recycling of expanded polystyrene from packaging. Progress in Rubber Plastics and Recycling Technology, 26(2), 83-92, (2010).
18. N. Nuraje, W.S. Khan, M. Ceylan, Y. Lie, and R. Asmatulu "Superhydrophobic Electrospun Nanofibers," *Journal of Materials Chemistry A*, Vol. 1, pp. 1929-1946, 2013.
19. R. Asmatulu, M. Ceylan, and N. Nuraje "Study of Superhydrophobic Electrospun Nanocomposite Fibers for Energy Systems," *Langmuir*, Vol. 27, No. 2, pp. 504-507, 2011.