Research Article

Salim Ok*, Julia Sheets, Susan Welch, Tingting Liu, Savas Kaya, and David R. Cole

Wetting behaviors of fluoroterpolymer fiber films

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Abstract: Various aspects of electrospun fibers prepared from terpolymer of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and vinylidene fluoride (VDF) (THV)/acetone solutions at two applied voltages, THV/acetone solutions having Texas montmorillonite with two ratios, and THV/ethyl acetate solutions using two needle sizes are described. Fibers from THV/acetone and THV/ethyl acetate solutions showed shallow indentations and pores, respectively. The clay, functioning as electrospinning agent, did not influence the fiber morphology, but yielded narrower fiber diameter distribution and the thinnest fibers. Heterogeneous fiber diameter distribution and increase in the fiber diameters were observed by lowering the voltage for fibers of THV/acetone solutions. Fibers from THV/ethyl acetate solutions had the largest diameter and the broadest diameter distribution. Electrospun THV fibers having both hydrophobic characteristics with nearly 140° water contact angles and oleophilic properties with oil contact angles less than 45° might have applications in areas such as water/oil separation.

Keywords: THV fluoropolymer, electrospinning fibers, hydrophobicity, oleophilicity, tuning morphology

1 Introduction

Typical fluoropolymers including poly(tetrafluoroethylene) (PTFE) and poly vinylidene fluoride (PVDF) have excellent

properties of resistance to chemicals such as strong acids and bases, hydrophobicity, and low friction coefficient (1). Some of the fluoropolymers such as classical aromatic fluorinated poly(2,3,4,5,6-penta-fluorostyrene) are electro-spinnable, where electrospinning parameters could change the morphology and hence hydrophobicity of the fibers (2).

There is sufficient interest in new types of fluoropolymers that can be processed by different techniques and that can exhibit advantageous chemical and physical properties similar to those of PTFE. The chemical stability of terpolymer of tetrafluoroethylene (TFE), hexafluoropropylene, and vinylidene fluoride (THV) (Figure 1) is comparable to that of PTFE (3). Among different THV grades available, THV-221 G is soluble in some organic solvents such as acetone and ethyl acetate (4). The solubility of THV-221 G in common organic solvents makes it an ideal fluoropolymer to test for fiber formation by electrospinning, an important task for fluoropolymers in terms of finding the most proper experimental conditions.

Electrospinning employs large electrical fields to draw a polymer solution from a spinneret to form fine fibers (5–7). The polymer solution is ejected toward a grounded collector such as a silicon wafer, and as the solvent evaporates, a sheet of fiber is formed where the jet stream lands. Fiber diameter, morphology, and surface properties may vary as a function of experimental parameters (8). Depending on the solution regime and rheology, the fiber-like structure is the result of significant chain entanglement. Insufficient chain entanglement in dilute regime results in small particulates (9). Electrospinning fluoropolymers might establish super water-resistant fiber thin films (2). Hence, such fluoropolymer-based electrospun fibers either in pure state or in mixture with inorganic materials might be applied in special coatings and membranes.

Inorganic materials such as montmorillonite clays, in electrospinning polymers, are sometimes added into polymer solution to improve the fiber properties (10). Montmorillonite, natural clay with swelling ability (11), has been utilized as a processing aid agent for polymer fiber formation by electrospinning (12). For example,

* Corresponding author: Salim Ok, Petroleum Research Center, Kuwait Institute for Scientific Research, P.O. box 24885, Safat, 13109, Kuwait, e-mail: sok@uos.de

Julia Sheets, Susan Welch, Tingting Liu, David R. Cole: School of Earth Sciences, The Ohio State University, Columbus, 43210, Ohio, USA

Savas Kaya: School of Electrical Engineering and Computer Science, Russ College of Engineering and Technology, Ohio University, Athens, 45701, Ohio, USA

Figure 1: Monomeric units of THV. HFP, hexafluoroethylene; VDF, vinylidene fluoride; TFE, tetrafluoroethylene.

Prince *et al.* showed that an increase in montmorillonite concentration influenced properties such as wettability of electrospun PVDF fibers (13). These authors also reported an increase in water contact angle of electrospun nanofiber membranes consisting of PVDF blended with clay nanocomposites as the clay concentration was increased. In the current study, one of the aims of adding Texas montmorillonite to the polymer solution is to study the potential of clay mineral as a processing aid additive in tuning properties of the fibers such as the diameter and if possible wettability type characteristics of the fibers.

Wettability is considered one of the most important properties of materials for both fundamental studies and practical applications (14). Among different materials, fluoropolymers form surfaces that effectively repel water (1). For fluoropolymers such as PTFE and PVDF as the surface tension decreases, water contact angle increases. The hydrophobic surfaces may also show oleophilic character. Materials with hydrophobic and oleophilic characters have potential to be used in processing the oil/water separation due to oil spills, an important environmental issue (15). In this regard, we need to mention that recently oil spills result in severe economic and environmental problems (16–19). Moreover, the oil containing wastewater in the routine life is a big scientific challenge because of additional contaminants such as heavy metals and organic dyes (18). Therefore, it is essential to find proper and efficient methods to solve this worldwide existing issue (17,19). Among different approaches in oil/water separation, membrane materials with differing interfacial characteristics of oils and water gain more interest (17).

Despite previous attempts to characterize THV, there are still limited data on THV properties, especially at solid interfaces. Although the electrospinning technique has been employed in polymeric fiber formation (6,7), there are only two short reports on electrospun THV fiber-like structures and fiber formation (20,21). Contrary to the report by Ok *et al.* (20) where the polymer solution concentration was varied from 8.4 to 20 wt%, the solution concentration was not varied in the present study, while solvent type, needle size, applied voltage, and feed rate

differed from the studies by Ok *et al.* (20) and Zhang *et al.* (21). Moreover, in the report by Ok *et al.* (20), Wyoming montmorillonite with low Mg was utilized, and in the present study, Ca-rich Texas montmorillonite has been used. In the study by Ok *et al.* (20), both “fiber-like” structures and “beans”-type fibers were observed, while in the present study, mainly smooth fibers were obtained, which will be discussed later. In the current report, besides measuring the hydrophobicity, oleophilicity of the fibers is also tested. Herein, the detailed analysis of average fiber diameter, not covered in the report by Ok *et al.* (20), is also shown.

This study focused on how the morphology, average diameter, and diameter distribution of the fibers are changed as a function of applied voltage, the chemistry of solvent, the needle size, and the amount of a clay mineral into the polymer solution. This leads to delineation of the experimental conditions required for better definition of electrospun THV fiber formation mechanisms in addition to better characterization of the fibers. Therefore, the goals of this study are as follows: (i) to reveal experimental conditions to form mainly fibers rather than fiber-like structures (20), (ii) to study whether there is any dependence of hydrophobicity of the electrospun THV fibers on any experimental parameter and test oleophilicity of the electrospun fibers, (iii) to check the possible influence of solvent in electrospinning the THV fibers, and (iv) to test whether Texas montmorillonite would function as a suitable additive for fabricating THV composite fibers for water removal from crude oil and as adsorbent matrixes for oil spill cleanup.

2 Methods

The terpolymer sample THV-221G was provided by DYNEON GmbH (Burgkirchen, Germany) as pellets and used without any further purification. N-type, P-doped [100] silicon wafers with a 625 µm thickness were purchased from University Wafer, USA, and used as a substrate. Texas montmorillonite (STx-1b; Gonzales County, Texas, USA) was purchased from the Clay Minerals Society. Acetone and ethyl acetate with 98% purity were purchased from Alfa Aesar and Sigma Aldrich, respectively. The solvents were used as received without any purification. Distilled water was used for contact angle measurements. For oleophilicity tests, Mobil1 fully synthetic commercial motor oil (SAE 15W-50 Motor Oil), a formulated product with surfactants and inorganic additives, was used.

THV solutions in acetone and ethyl acetate were prepared with 15 wt% (THV:solvent/wt:wt), which produced solutions with viscosities sufficient for the experiments (see Table S1 in Supplementary material indicating viscosities of the solutions in Supporting Information). These two solvents with different volatilities (acetone > ethyl acetate) are used to compare the effect of solvent volatility on the properties of fibers. Montmorillonite (STx-1b), a Ca^{2+} rich clay, was added into the 15 wt% THV/acetone solution with two different weight ratios of polymer:clay (wt:wt/10:1) and (wt:wt/5:1). The amount of montmorillonite to be added into the polymer solution was determined referring to the previous report by Ok et al. (20). The polymer–clay solution was mixed thoroughly with a magnetic stirrer bar for 30 min to disperse the clay (till having milky solution due to white color of the clay) into the polymer–solvent mixture before electrospinning the fibers (see Table 1 summarizing the experimental conditions and the corresponding figures of the results).

The THV fibers were produced by the electrospinning apparatus built in the Kaya laboratory of Ohio University (see Figure S1 in Supplementary material showing and explaining the details of the electrospin apparatus). The polymer solution was taken in a 1.6 mL hypodermic plastic syringe and forced out of a 22-gauge needle for polymer/acetone solutions, both 16-gauge and 11-gauge needles for polymer/ethyl acetate solutions, and both 16-gauge and 22-gauge needles were utilized for polymer/acetone solutions with montmorillonite (STx-1b) added at 19 kV. Syringe pump feed rate was 1.1 mL/h. The needle-to-collector (silicon wafer) distance was kept constant at 15 cm. Electrospinning was performed at two different voltages, 19 and 16 kV, for polymer/acetone solution, and kept constant at 19 kV for polymer/ethyl acetate solution and polymer/acetone plus clay solution. Attempts to electrospin fibers from THV/ethyl acetate solution using the 22-gauge needle led

to very slow flow of the polymer solution and the associated bulging of the polymer solution at the mouth of the needle, which did not allow the formation of the fibers. To test only wetting behaviors, fibers were also electrospun from either acetone or ethyl acetate solution with different feed rates and applied voltage by keeping distance to the collector at 15 cm and using 22-gauge needle (see Table S2 in Supplementary material).

The morphology of the electrospun THV fibers was characterized with scanning electron microscopy (SEM), using a FEI Quanta 250 Field Emission Gun SEM (in the OSU Subsurface Energy Materials and Characterization Laboratory). SEM samples were lightly coated with Au/Pd using a Denton Desk V sputter coater for 45 s. Hydrophobicity and oleophilicity of the samples were analyzed by contact angle measurement. Samples were analyzed using a sessile drop method on an Easy Drop goniometer (Department of Materials Science, The Ohio State University) equipped with a Teli-Toshiba CCD camera at 25°C. A total of 5–15 μL of deionized water was placed onto different regions of the electrospun films to test the influence of topography in the fiber films as a single drop, and a screenshot was taken after 3 s. Easy Drop software (DropShape Analysis-Registered Version) was utilized to calculate a contact angle based on the screenshot using linear baseline. Three measurements were taken for each sample, and an average value of the three measurements was recorded. Oil drop measurements were conducted under the same conditions.

Average fiber diameter and fiber diameter distributions were analyzed using at least four different SEM images acquired from each sample. Dozens of fibers from each SEM image were selected, and a line was drawn three times across each fiber to measure the fiber width using the *Analyze* → *Measure* function of the software ImageJ 1.47v following the procedure proposed by Chen et al. (22). Three measurements per fiber were done, and the values

Table 1: Experimental conditions and corresponding figures for the results. Concentrations of THV/solvent solutions are 15 wt%

Solvent	Needle size	Applied voltage (kV)	Figure numbers
(1) Acetone	22 gauge	19	2 and 3
(2) Acetone	22 gauge	16	2 and 3
(3) Ethyl acetate	16 gauge	19	4 and 5
(4) Ethyl acetate	11 gauge	19	4 and 5
(5) Acetone, THV/montmorillonite: 10/1	16 gauge	19	6 and 7
(6) Acetone, THV/montmorillonite: 5/1	16 gauge	19	6 and 7
(7) Acetone, THV/montmorillonite: 10/1	22 gauge	19	6 and 7
(8) Acetone, THV/montmorillonite: 5/1	22 gauge	19	6 and 7

were averaged. Then, the number of fibers in each specific fiber diameter range was summed to produce histograms showing the fiber diameter distribution.

3 Results and discussion

3.1 Changes in fiber morphology, average diameter, and fiber diameter distribution by various parameters

There are two different applied voltages, two solvents, three needle types, and two different ratios of solvent/clay tested for electrospinning THV fibers in this study. As a result, different observations were made on diameter, average diameter, morphology, and contact angle of the electrospun THV fibers. Table 2 presents a systematic summary of the observations.

3.1.1 Effect of applied voltage

Fibers produced with an applied voltage of 19 kV from 15 wt% THV/acetone solutions with the 22-gauge needle (sample 1 as numbered in Tables 1 and 2 and Figure 2a and b) occur as flattened and twisted strips with measured diameters ranging from 0.40 to 2.60 μm . Many of the fibers have linear or small shallow indentations. A shriveled surface morphology of the fibers is also frequently observed (Figure 2b). Nearly 37% of the fibers range in diameter between 0.6 and 0.8 μm . Less than 15% of the fibers have diameters larger than 1.2 μm (Figure 3).

The fibers produced at the lower applied voltage of 16 kV from 15 wt% THV/acetone solutions with the 22-gauge needle (sample 2, Figure 2c and d) have some fibers that are similar to those prepared in the 19 kV experiment, whereas others have a larger diameter and are covered with a fairly uniform distribution of small indentations. The fiber diameter ranged approximately between 0.87 and 3.24 μm (Figure 3). The mean diameter of the fibers in the THV/acetone solution experiments increased, and the fiber size distribution changed as the voltage was decreased. When the voltage was reduced to 16 kV, the diameter range of the majority of the fibers ($\geq 85\%$) shifted from the region of 0.4 and 1.2 μm to the region between 1.2 and 2.2 μm . The fiber diameter range exhibiting the greatest abundance is from 1.4 to 1.6 μm in the case of the 16 kV applied voltage, and nearly 25% of the fibers have diameters in this range. The thickest

fibers with diameters larger than 2.6 μm comprise only approximately 10% of the fibers.

One of the important properties of the electrospun THV fibers produced with variable applied voltage is their morphology. While many of the smaller fibers have relatively smooth surfaces, others have elongated shallow surface indentations. Most of the larger fibers generated in the 16 kV treatment have abundant shallow dents covering their surfaces (Figure 2). The morphology of electrospun THV fibers exhibited both similarities and differences with respect to electrospun fibers of poly(VDF-co-HFP). The poly(VDF-co-HFP) electrospun fibers exhibited fully interconnected porous structure for the concentrations of 12–18 wt% in acetone/dimethylacetamide (in varying ratios of 3:7, 5:5, and 7:3, w/w) and applied voltage of 11, 18, and 24 kV (23), while in this study, when the fibers were electrospun from THV/acetone solution, no porous structure in fibers was observed. This indicates that the indentations do not penetrate through the fiber surfaces. In this regard, the morphology of THV fibers electrospun from acetone solution is different from that observed in the study by Li *et al.* (23). Compared to the report by Ok *et al.* (20) where there were hollow and beaded fibers observed, in this study, fibers show flattened, twisted strips, and shriveled surface as well as small shallow indentations (see Table 2 for details). The common feature in the morphology of the fibers in this study and the previous study by Ok *et al.* (20) is the porosity, which is observed only in the case where the fibers were electrospun from THV/ethyl acetate solution. This shows that when ethyl acetate is used as a solvent, mostly porous structures are to be observed in the morphology of the THV fibers to be generated by electrospinning.

Li *et al.* showed that electrospinning poly(VDF-co-HFP) using 16 wt% solutions in acetone:DMAc (w/w: 7/3) produced different ranges of polymer fiber diameter when the applied voltage was changed (23). The thickest fibers (3.8 μm) were obtained at 24 kV, while the applied voltage of 11 kV yielded the thinnest fibers (down to 0.1 μm diameter). In contrast, in this study, thicker fibers were observed when the applied voltage was decreased to 16 kV during electrospinning. Elongate poly(VDF-co-HFP) electrospun fibers parallel to each other with regular diameters of 0.8–1.0 μm were obtained at 15 wt% polymer solution concentration in acetone/DMAc (7:3 by weight ratio), 15 cm distance to the collector, 2 mL/h of flow rate, and 14 kV of applied voltage (24). In this study, we also observe fiber diameters in the range of 0.8–1.0 μm but at low abundance. The fraction of the fibers with diameters in the range of 0.8–1.0 μm was reduced from approximately

Table 2: Summary of the results on fiber size distribution and diameter, morphology, and wetting affected as a function of voltage, solvent/needle type, and clay additive. SEM images were analyzed by ImageJ 1.47v. Bulging of the polymer solution at the mouth of the needle does not allow electrospinning THV fibers from THV/ethyl acetate solution when 22-gauge needle

Sample #		Fiber size distribution (μm)	Average fiber size diameter (μm)	Morphology	Wetting contact angle ($^\circ$)
1	Voltage: 19 kV Solvent/needle type: acetone/22 gauge Clay additive: — Voltage: 16 kV	0.40–2.60	0.88 ± 0.44	Flattened, twisted strips, shriveled surface	141
2	Solvent/needle type: acetone/22 gauge Clay additive: — Voltage: 19 kV	0.87–3.24	1.73 ± 0.53	Flattened, twisted strips, shriveled surface Small indentation	132 <20
3	Solvent/needle type: acetone/22 gauge Clay additive: — Voltage: 19 kV	0.72–5.43	1.92 ± 1.23	Pronounced pore-like structures	141
4	Solvent/needle type: ethyl acetate/16 gauge Clay additive: — Voltage: 19 kV	0.49–6.33	1.80 ± 1.73	Pronounced pore-like structures	139 43
5	Solvent/needle type: ethyl acetate/11 gauge Clay additive: — Voltage: 19 kV	0.31–2.24	0.92 ± 0.37	Small shallow indentations	140
6	Solvent/needle type: acetone/16 gauge Clay additive: THV/montmorillonite: 10/1 10 wt% clay Voltage: 19 kV	0.29–3.05	0.80 ± 0.40	Small shallow indentations	139
7	Solvent/needle type: acetone/16 gauge Clay additive: THV/montmorillonite: 5/1 20 wt% clay Voltage: 19 kV	0.21–1.03	0.50 ± 0.14	Small shallow indentations	138
8	Solvent/needle type: acetone/22 gauge Clay additive: THV/montmorillonite: 10/1 10 wt% clay Voltage: 19 kV	0.25–1.09	0.48 ± 0.13	Small shallow indentations	134
	Solvent/needle type: acetone/22 gauge Clay additive: THV/montmorillonite: 5/1 20 wt% clay

Figure 2: SEM images showing electrospun THV nanofibers prepared from the THV/acetone solution with the concentration of 15 wt%; 15 cm₂₂ gauge₁₉ kV, sample 1 as listed in Tables 1 and 2 (a and b) and 15 cm₂₂ gauge₁₆ kV, sample 2 as listed in Tables 1 and 2 (c and d).

17%–6% when the applied voltage was reduced to 16 from 19 kV. The electrospun THV fibers prepared from THV/acetone solution at the applied voltages of 19 and 16 kV have a heterogeneous fiber diameter distribution compared to the poly(VDF-co-HFP) electrospun fibers prepared by Kim *et al.* (24). These differences could be attributed to differences of the solvents used—acetone/DMAc versus acetone—and the chemical structure of the two polymers where THV contains additional TFE units in the terpolymer backbone.

The effect of changing applied voltage on the average fiber diameter and fiber diameter distribution of the fibers produced has been tested previously. The

results of these studies are inconsistent, in that both an increase (25) and a decrease (26) in fiber diameter with the increasing voltage are reported. These discrepancies were explained by the difference in electrospinning parameters and polymer solutions used during experiments (27). In general, a higher applied voltage ejects more fluid in a jet, resulting in a larger fiber diameter (28). In our case, applying a higher voltage decreased the average fiber diameter of THV when the fibers were fabricated from THV/acetone solution by using 22-gauge needle. Zhang *et al.* produced THV fibers by dissolving THV 221 GZ in dimethylformamide (DMF) with 15 wt% concentration and with spinning time of 12 h (21).

Figure 3: Histogram of fiber diameter distribution for the fibers prepared from 15 wt% THV/acetone solution.

Varying the applied voltage from 10 to 20 kV and even to 25 kV did not change the average fiber diameter significantly and obtained average fiber diameter around $1.40\ \mu\text{m}$ with a standard deviation of $\pm 0.55\ \mu\text{m}$ (21). The effect of applied voltage in this study also contradicts the general expectation, but is consistent with some of the previous studies (14,29,30).

THV investigated in this study showed 38.2, 10.4, and 51.4 mole percentage of VDF, HFP, and TFE, respectively (31). Quantitative analysis of the ^{19}F NMR spectrum of THV-221 G shows that 50% of TFE units are adjacent to each other, while 90% of HFP groups are closer to VDF units (32). Furthermore, the critical molar mass (M_c) for the entanglement of random branches of THV (having 39% TFE, 11% HFP, and 50% VDF) equals 2.5 times the molar mass of entanglements M_e ($M_c = 2.5 M_e$), while M_e of THV was determined as 4,100 g/mol (33). M_c for the entanglement is important because polymer chain entanglement in solution strongly influences the fabrication of polymeric fibers by electrospinning.

Ahmed et al. reported that, on average, electrospun poly(VDF-co-HFP) fiber diameters increased as the concentration of the polymer solution increased for a given applied voltage. For the given polymer concentration, an increase in the applied voltage did not show systematic changes in the average fiber diameter. When 14 wt% of poly(VDF-co-HFP) and 70/30 DMAc/acetone solution were used, the average fiber diameter of $611 \pm 276\ \text{nm}$

was obtained at 13 kV, whereas the fiber diameter of $606 \pm 116\ \text{nm}$ was obtained at 17 kV, without a significant difference in the average fiber diameter (34). Conversely, in this study, the average fiber diameter was lowered by an increase in the applied voltage (Table 2). THV/ethyl acetate solutions with various concentrations were utilized by Ok et al., and only 20 wt% solution at the applied voltage values of 20 and 25 kV yielded bean-type fibers by electrospinning. At all other conditions, only fiber-like structures were observed (20). In this study, it was possible to obtain THV fibers even at lower applied voltage values. These comparisons also indicate the optimum experimental conditions and parameters such as solvent type and applied voltage for fabricating THV fibers by electrospinning.

3.1.2 Effects of solvent type and needle size

One of the most important issues in polymer solutions is the interaction between polymer and solvent. The polymer/solvent pair determines viscosity of the solution, which in turn affects how the polymer could be processed by electrospinning (see Table S1 showing the viscosities of THV solutions). As shown in Table S1 in Supplementary material, THV/ethyl acetate solution had the highest viscosity, and this solution yielded the thickest fibers. The addition of clay mineral increased

Figure 4: Representative SEM images showing electrospun THV microfibers prepared from the THV/ethyl acetate solution with the concentration of 15 wt%; 15 cm₁₁ gauge₁₉ kV, sample 3 as listed in Tables 1 and 2 (a) and 15 cm₁₆ gauge₁₉ kV, sample 4 as listed in Tables 1 and 2 (b). Yellow arrows show the pores.

the viscosity of THV/acetone solution compared to THV/acetone solution without montmorillonite. These viscosity values show that solvent type should influence the viscosity and hence properties of the electrospun fibers. Therefore, ethyl acetate was used to observe the effect of solvent on the electrospun THV fibers. When ethyl acetate was used as a solvent, there was greater heterogeneity observed in the measured fiber diameters, and overall larger fibers (from 0.49 to 6.33 μm [samples 3 and 4]) were produced (Figure 4) compared to those fabricated with THV/acetone solution. The larger fibers in the ethyl acetate treatment exhibited pronounced pore-like structures as opposed to shallower indentations on their surfaces (see yellow arrows on Figure 4 showing the pores).

The fiber diameter produced from THV/ethyl acetate solution was broader than the fibers prepared from THV/acetone solution (Figure 5). For the experiments conducted with the 16-gauge needle (sample 3 as numbered in Tables 1 and 2), the fibers had a size distribution between 0.72 and 5.43 μm . Nearly 20% of the fibers produced using the 16-gauge needle were within the 1.0 and 1.2 μm size fraction, while only 5% of the fibers were greater than 3.6 μm . When the needle size was increased to 11-gauge, a larger number of thicker fibers were formed, and a fiber diameter as wide as 6.33 μm was observed. The fiber diameter range with the greatest frequency produced from the 11-gauge needle (sample 4

as numbered in Tables 1 and 2) is between 0.6 and 0.8 μm with the fraction of nearly 14%, while the percentage of the thickest fibers more than 3.6 μm increased to approximately 12%.

The pore-like surface structures may be related to the stretching of the polymer chains and a quasi-Newtonian flow, in which fully stretched chains flow past each other, leading to a constant elongational viscosity (35). Another explanation for the pore-like structures is phase separation into polymer-rich and polymer-poor regions. There is a high probability that polymer-poor regions would lead to the formation of such pores (6). In this study, varying the solvent changed the surface morphology in terms of the forming porous structure, in particular, when fibers are produced from THV/ethyl acetate solutions at 19 kV, and needles of 16-gauge and 11-gauge are used. As suggested previously, bulging clogs up the smaller needle and thus does not allow electrospinning THV fibers from THV/ethyl acetate solution when 22-gauge needle is used. However, in the short report by Ok *et al.* (20), THV fiber-like structures were prepared by electrospinning using ethyl acetate as a solvent and a 22-gauge size needle. The concentrations of the THV/ethyl acetate solutions were 8.4, 12, 15, and 20 wt%. The observed fiber-like structures and fibers with string bean-type shape showed porous morphology, very similar to those produced in the current structure. This indicates that the porous morphology in the electrospun THV fibers fabricated from THV/ethyl

Figure 5: Histogram of fiber diameter distribution when the fibers were prepared from 15 wt% THV/ethyl acetate solution.

acetate solutions is independent of the THV/ethyl acetate solution concentration. In addition, porosity was observed in electrospun THV fiber-like structures, string bean-type fibers obtained previously (20), and as well as the elongate fibers of this study. This means that the porosity is also independent of the fiber morphology itself. Li et al. observed that changing the solvent ratio of acetone to DMAc had less influence on the morphology of the fibers than did polymer concentration and applied voltage (23). Zhang et al. also studied the effect of solvent on the mean pore size, porosity percentage, and fiber diameter among some other parameters. As going from 50%–50% weight percentage DMF–acetone to 100% DMF, the mean pore size decreased from 1.24 to 0.79 μm, while the porosity percentage increased from 42.1% to 55.6% and the average fiber diameter decreased from 2.52 to 1.34 μm (21). Using acetone as a solvent led to an increase in the average fiber diameter, an increase in the mean pore size, and a decrease in the porosity percentage. On the contrary, in this study, the thickest fibers were electrospun from THV/ethyl acetate solutions. The fibers prepared from THV/ethyl acetate solutions with the largest fiber diameter distribution are explained by both the larger needle size and the type of solvent.

To summarize the change in morphology of electrospun THV fibers, we suggest that both applied voltage and solvent type have effects on the morphology of the fibers. In the case of THV/acetone solutions, when the applied voltage was lowered, there were small indentations observed in the morphology of the electrospun THV fibers.

When the solvent was changed to ethyl acetate, porous fibers were obtained. It is obvious that the effect of the applied voltage is less, while the effect of the solvent is more pronounced. In addition, using ethyl acetate as the solvent thickens the average THV fiber diameter.

3.1.3 Montmorillonite addition

It is well known that the addition of clays such as montmorillonite affects the properties of polymer-based materials including electrospun polymeric fibers (10–13). Montmorillonite may function either as a filler or an electrospinning aid agent by, for example, changing the viscosity of the polymer solution. In this context, we tested how the addition of Texas montmorillonite into the polymer solution influenced properties such as the average diameter of fabricated THV fibers. Texas montmorillonite was added to the THV/acetone solution to determine the effect of a hydrophilic clay surface on fiber formation and properties. Experiments with clay addition were done under the similar conditions as in the case of samples 1 and 2 where THV was dissolved in acetone, 15 wt%, 15 cm, etc. Experiments with clay addition were conducted at two different THV:clay ratios of 5:1 and 10:1. Elongate fibers show regular morphology with small shallow indentations (samples 5 and 6, Figure 6). SEM images shown in Figure 6 reveal that the fibers have narrower diameter distributions. Figure 7 shows that when montmorillonite is added and a 16-gauge needle is

used (samples 7 and 8), relatively thinner fibers are obtained with respect to the fibers produced from terpolymer solutions in the pure state without clay. Occasionally, fibers are wider where a clay particle is engulfed within a fiber (Figure 6). The addition of clay into the polymer solution did not change the morphology of the electrospun fibers significantly compared to the control experiments without clay. However, the average fiber diameter and fiber diameter distributions were affected when the fibers were electrospun from clay mineral added THV/acetone solution compared to those in treatment 1 conducted under similar condition without clay. The major difference observed in the SEM images is that the distribution of the filaments in these treatments with the addition of clay mineral into the polymer solution is very sparse compared to the other samples prepared without clay addition.

Changing the THV-to-montmorillonite ratio does not influence the distribution of fiber diameters significantly, as shown in Figure 7. The thinnest fibers and narrower fiber diameter distributions are observed when the natural clay is utilized. The fiber diameter distribution with the polymer to clay ratio of 10:1 was between 0.30 and 2.30 μm when 16-gauge was used for electrospinning the THV fibers (sample 5). The fiber diameter range with the greatest frequency produced from clay-added THV/acetone solution with the polymer-to-clay ratios of 10:1 and 5:1 is between 0.6 and 0.8 μm , and the fraction of the fibers in this range decreases from 34.3% to 26.8% when the ratio is changed from 10:1 to 5:1 (sample 6). This suggests that when more clay is added to the solution, the fraction of thinner fibers does not change significantly. The percentage of the thickest fibers more than 1.6 μm is much less than 5% in the case of the both polymer-to-clay ratios.

When 22-gauge needle was utilized in electrospinning fibers from acetone/THV/montmorillonite blends, the fiber diameter distribution with the polymer-to-clay ratio of 10:1 was between 0.21 and 1.03 μm (sample 7). The fiber diameter range with the greatest frequency produced from the clay-added THV/acetone solution with the polymer-to-clay ratios of 10:1 and 5:1 is between 0.4 and 0.6 μm , and the fraction of the fibers in this range increases from 56% to 63% when the ratio is changed from 10:1 to 5:1 (sample 8). This suggests that when more clay is added to the solution, the fraction of thinner fibers increases only slightly. The percentage of the thickest fibers more than 0.8 μm is much less than 5% in the case of the both polymer-to-clay ratios. This indicates that the addition of clay led to thinner THV fibers during electrospinning, as suggested by Neppalli *et al.* (12).

A comparison of Figures 2 and 6 suggests that the addition of montmorillonite yielded relatively thinner fibers. Increasing the ratio of polymer to clay did not influence the average fiber diameter or fiber diameter distribution dramatically. When the THV to montmorillonite ratio was varied, the results were similar (Figure 6a and b), suggesting that the hydrophilic clay surfaces had a little impact on the fiber formation and morphology/surface characteristics (Table 2).

The addition of montmorillonite into the THV/acetone solution increased the solution viscosity resulting in differences in the distribution of fiber diameters. For example, Li *et al.* reported that the addition of organically modified montmorillonite (MMT) resulted in a 60% higher viscosity for nylon-6 polymer solutions compared to clay-free preparations (36). The analysis of SEM images of nylon-6 fibers from 20% solution of nylon-6/88% formic acid showed that 80% of the fibers have diameter between 120 and 180 nm, and only 6% of the fibers have a diameter greater than 500 nm. Conversely, 20% solution of nylon-6/modified MMT/88% formic acid yielded much thicker fibers. Only 7% of the fibers have a diameter of 200 nm, while diameters of almost 90% of the fibers range between 300 and 600 nm. This increase in the fiber diameter distribution could be related to the increase in the viscosity of the clay added solutions (36). In this study, a contrary result is observed. The addition of MMT into THV/acetone solution yielded thinner fibers. This contrary result with respect to the report by Li *et al.* (36) is attributed to two factors: (i) chemistry of the polymer and clay of interest and (ii) the method of blend preparation. Nylon-6 is not a fluoropolymer, whereas we electrospun a fluorinated terpolymer. We used a natural montmorillonite, whereas Li *et al.* worked with organically modified montmorillonite (Cloisite-30 B). Li *et al.* blended nylon-6 and Cloisite-30 B using a twin-screw extruder operating at 250°C (36), while we blended THV and the clay by continuous stirring with a magnetic bar in the solvent.

In this study, the weight percentage of the added clay in the polymer solution was 10% and 20%. A higher viscosity was expected when the clay was added into the THV/acetone solutions. Therefore, the needle with a larger gauge (16-gauge) size was used for electrospinning fibers from montmorillonite added THV/acetone solutions. This is the only experimental difference compared to the experimental conditions of fiber formation from THV/acetone solutions. This needs to be taken into account while comparing the morphology and the mean diameter of the fibers prepared from solutions with and without clay.

Neppalli *et al.* studied the effect of Cloisite 20A, a montmorillonite organically modified by dimethyl-dihydrogenated

Figure 6: SEM images showing electrospun THV fibers prepared from the THV/acetone solution with source clay standard Texas montmorillonite (STx-1b). (a) Sample 5 as listed in Tables 1 and 2 (THV:montmorillonite/10:1) and sample 6 as listed in Tables 1 and 2. (b) (THV:montmorillonite/5:1) prepared with 15 cm₁₆gauge₁₉ kV, SEM images taken by back-scattered electron detector (BSED); and sample 7 as listed in Tables 1 and 2. (c) (THV:montmorillonite/10:1), sample 8 as listed in Tables 1 and 2. (d) (THV:montmorillonite/5:1), prepared with 15 cm₂₂gauge₁₉ kV, SEM images taken by the Everhart–Thornley detector. (a, c, and d) Examples of clay in the fibers. (b) Example of clay on fibers indicated with the circle.

tallow quaternary ammonium, on the polymorphism, structure, and morphology of PVDF (12). The PVDF/DMF solutions contained 3% and 5% Cloisite 20A with respect to PVDF. Electrospinning did not significantly disperse the clay with the fiber matrix, rather clay acted as a processing aid agent inhibiting the formation of beads in the fibers. Clay and electrospinning process favored the β phase of PVDF. Neppalli et al. claimed that clay eases electrospinning of fluoropolymer by increasing the solution conductivity. They also showed that the average

diameter of the PVDF fibers increased approximately twofold by the addition of clay into the polymer solution (12). The largest average PVDF fiber diameter was between 140 and 160 nm in the study by Neppalli et al., while in this study, the largest average diameter of the fibers prepared by electrospinning from THV/acetone solutions is between 1.0 and 1.2 μm . The average fiber diameter of the fibers obtained from clay added polymer solutions is approximately 500 nm, and this is almost five times larger average fiber diameter with respect to the

Figure 7: Histogram of fiber diameter distribution when the fibers were prepared from 15 wt% montmorillonite added THV/acetone solution: (a) 16-gauge and (b) 22-gauge.

electrospun fibers obtained from Cloisite 20A added PVDF solutions in dimethylformamide. Comparing the properties such as the fiber diameter of electrospun THV fibers with respect to other electrospun fluoropolymer fibers such as those of PVDF demonstrate the unique properties of electrospun THV fibers.

3.2 Wetting properties of fibers

Wetting characteristics of the THV fibers were also studied with two different liquids: water and synthetic oil (Mobil1 SAE 15W-50 Motor Oil). The major goal was to determine the “phobic” or “philic” characters of the

Figure 8: Representative profiles of water droplets on electrospun THV fibers prepared from the following solutions: (a) sample 1: THV/acetone 15 wt%: 15 cm₂₂ gauge₁₉ kV. (b) Sample 5: THV/acetone 15 wt% with THV:montmorillonite/(10:1) 15 cm₁₆ gauge₁₉ kV. (c) Sample 3: THV/ethyl acetate 15 wt% 15 cm₁₆ gauge₁₉ kV.

electrospun THV fibers in two different liquids. Clarification of wetting behaviors of the THV fibers is useful when designing novel applications for the THV fibers. As shown in Table 2 and Figure 8, the contact angle of water on THV fibers ranged between 132° (sample 2) and 141° (sample 3), where the water droplet

was placed onto areas having fibers with high density. Moreover, samples 2 and 4 had the contact angles of <20° and 43°, respectively, toward synthetic oil (Mobil1 SAE 15W-50 Motor Oil; Table 2).

3.2.1 Hydrophobicity

Super hydrophobic surfaces, having static water contact angle of 150° or higher and a shedding angle of less than 10°, are obtained by proper control of roughness and energy of the surface of interest (37), and are of great interest in many research areas (38). Young's equation (39) describes the contact angle (θ) of a fluid such as commonly utilized water (40) on a solid surface in terms of the interfacial tensions between the three phases:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \times \cos \theta \quad (1)$$

where γ_{sv} is solid–vapor interfacial tension, γ_{sl} is the solid–liquid interfacial tension, and γ_{lv} is the liquid–vapor interfacial tension. Wenzel (41) and Cassie–Baxter (42) models give a basic description of how a static water contact angle can be increased by changing surface roughness in homogeneous and heterogeneous wettings, respectively (see schematic shown in Figure 9 summarizing the two states of wetting).

According to Wenzel's model, the liquid on the solid surface penetrates completely into the grooves of the roughened surface (41,43), increasing the area between the water–liquid interfaces. According to Cassie's model, the contact area between water and air is maximized forcing water to form spherical droplets (42).

The fibers have such hydrophobic character, which is slightly below the limit for super hydrophobic surfaces (>150°), being independent of the fiber diameter range. The fibers prepared from the polymer solution in acetone with the natural clay demonstrated similar hydrophobic character (Table 2). Cassie's model is more appropriate for explaining the near super hydrophobic character of the electrospun THV fibers studied here. The water droplet did not fill the grooves between the surfaces of THV fibers because the water did not go into the indentations observed in the morphology of the fibers.

In this study, the highest contact angle of water measured on the electrospun THV fibers was 141° (sample 3); therefore, we prefer using the expression “slightly below super hydrophobic limit (>150°)” in explaining the hydrophobic character of the THV fibers. As presented in Table S2 in Supplementary material, when applied voltage was 20 kV and flow rate was

Figure 9: Schematic representations of Young, Wenzel, and Cassie–Baxter states of liquids on solids. θ is the apparent contact angle corresponding to the stable equilibrium state.

varied, it was still possible to keep the contact angle toward water around 140° on the THV fiber thin films. Therefore, we suggest that using either acetone or ethyl acetate as a solvent results in “slightly below super hydrophobic limit” electrospun THV fibers, while the applied voltage and flow rate of the terpolymer solutions do not influence the hydrophobicity of the THV fiber films significantly. The contact angles of the current study are approximately 10° higher compared to the results by Zhang *et al.* (21) and match the previous results of Ok *et al.* (20). This shows that slightly below super hydrophobicity ($>150^\circ$) character of the electrospun THV fibers is reproducible and independent of most of the experimental parameters including solvent type and applied voltage compared to the previous reports (20,21), as well as the morphology of the electrospun fibers.

Prince *et al.* (13) showed that as the Cloisite 20A concentration increased, the contact angle of PVDF–clay nanocomposite electrospun fiber membrane also increased, and thus, PVDF–clay-based membrane had the highest water contact angle of $154.20^\circ \pm 3.04^\circ$. In another study on electrospinning zein, a hydrophobic protein produced from maize and hydrophilic montmorillonite composites, the contact angle of the electrospun fiber mats decreased from 133° to 95° with increasing amounts of montmorillonite (44). In contrast to both of these studies, in this study, no increasing or decreasing trend in the contact angle of THV/clay electrospun fibers was observed.

Super hydrophobicity on a surface is achieved by the low surface energy of the materials used, and roughness, both at the micro and nanometer scale, and the heterogeneity of solid surfaces. The high fluorine content of a polymer results in lower surface energy, resulting in higher contact angles (45). Rougher surfaces usually show higher contact angles with water (46). Contact angles can be changed by roughness in two ways. First, the surface area of the solid is increased by roughness. When a liquid is placed on a rough surface, the magnitude of solid–vapor interface replaced by solid–liquid interface

is larger than it would be on a flat surface (43). The possibility of tuning hydrophobicity of THV-221 G at solid interfaces in thin films prepared by the nonsolvent method was shown in the previous study (31). Polymer films produced by the nonsolvent method from the THV/ethyl acetate solution by using chloroform as the nonsolvent had an approximately 25% increase in the water contact angle compared to the solution casted films from THV/ethyl acetate solutions. This increase in the water contact angle was attributed to the increase in roughness of the THV-221 G films (31). In the report by Zhang *et al.* (21), the lowest contact angle (110°) for water was measured on the fiber membranes obtained from 10 wt% THV solution in 100% DMF at 15 kV applied voltage. All the other contact angles for water on the electrospun THV fiber membranes were between 125.6° and 131.4° , lower than the values of the present report. In another recent study, Ok *et al.* showed 43% increase in hydrophobicity of THV in thin films prepared by casting from mixed solvent (acetone) and nonsolvent (ethanol) (47).

X-ray photoelectron spectroscopy (XPS) measurements were conducted to clarify the contribution of lower surface energy groups to the observed hydrophobicity of the thin films. From XPS, it was determined that THV thin films prepared by casting from a good solvent (the solvent that is able to dissolve the terpolymer) and exhibiting hydrophobicity with water (contact angle around 100°) had very low or essentially zero percentage of $-\text{CF}_2$ and $-\text{CF}_3$ groups at the top most layers of the films. Conversely, the percentage contributions of the same lower surface energy functional groups in the XPS spectra of the THV thin films prepared from mixed solvent and nonsolvent were higher than the corresponding ones prepared by casting from a good solvent (47). Similar to the previous study on THV thin films (31), there was also direct correlation observed between roughness and hydrophobicity of THV thin films by atomic force microscopy (47). In this study, the indentations increased the roughness, which in turn

Figure 10: Representative profiles of motor oil (SAE 15W-50 synthetic Motor Oil) droplets on electrospun THV fibers prepared from the following solutions: (a) sample 4: THV/ethyl acetate 15 wt%: 15 cm₁₁ gauge₁₉ kV. (b) Sample 2: THV/acetone 15 wt%: 15 cm₂₂ gauge₁₆ kV (b). Contact angle is (a) 42.6° and (b) less than 20°.

increased the water contact angle. The second effect of roughness arises from energy barriers formed by the local slope of the rough surface changing the local contact angle. The energy barriers formed this way block the spreading or retraction of the liquid front (48). The Wenzel state is at a lower energy state. However, there is an energy barrier for a droplet to transition to the Wenzel state. Consequently, the drop can switch from one equilibrium state to another only if the drop can overcome the energy barrier between the two states (49,50). The energy barrier might explain the “near and below super hydrophobic” character of the electrospun THV fibers. Although the Wenzel state was favored due to lower energy, the energy barrier was not overcome so that the water droplet on the electrospun THV fibers

remained at the Cassie–Baxter state. The Cassie–Baxter state was preferred to the Wenzel state because air regions were still thermodynamically stable and water did not infiltrate the surface (42).

3.2.2 Oleophilicity

The tested property of electrospun THV fibers was their oleophilicity. As shown in Figure 10, the electrospun THV fibers prepared from THV/acetone and THV/ethyl acetate solutions showed oleophilicity with contact angles less than 45° (samples 2 and 4, see Table 2). The electrospun THV fibers prepared from the THV/ethyl acetate solution had an oil contact angle of 42.6°. The electrospun THV fibers had oil contact angle less than 20° when the fibers were prepared from the THV/acetone solution (Figure 10).

Synthetic oil (Mobil1 SAE 15W-50 Motor Oil) wets the electrospun THV fibers completely. Besides developing new super hydrophobic surfaces, the oil/water separation process and water preservation are important applications (51). Materials with both hydrophobic and oleophilic characteristics are chosen for oil collection since they permit disposing oil properly and minimize secondary pollution (51). In developing polymer-based hydrophobic and oleophilic systems, Feng et al. reported fabrication of polymer thin films from PTFE showing both super hydrophobic and superoleophilic characters (52). The unfortunate occurrence of oil spills polluting water is considered as a major challenge for natural environments (53). There have been various materials such as absorbents developed for cleaning oil spills (54). Among oil absorbents used in oil cleaning, synthetic polymers have numerous advantages such as high uptake capacity, fast adsorption kinetics, hydrophobicity, oleophilicity, and easy recovery from absorbents (53). For effective oil–water separation, both hydrophobic–oleophilic “oil-removing” surfaces and hydrophilic–oleophobic “water-removing” surfaces were studied (55).

There were reports describing the high oil absorption capacities of polystyrene (PS) electrospun fibers (56,57). However, due to its nonpolarity, PS fibers can be dissolved in gasoline. PS fibers also have poor mechanical stability and can be dispersed in oil after single usage. As a result, it is essential to apply such a system that is mechanically stable and nonsoluble in organic mixtures such as diesel having 75% saturated hydrocarbons and 25% aromatic hydrocarbons (51). In this regard, THV fibers showing both hydrophobic and oleophilic properties have potential for developing new

and novel systems for effective oil–water separation. Moreover, the THV fibers prepared by electrospinning might have applications as oil absorbent material in oil spill cleanup. Bruno also noted that fluoroplastics with high fluorine contents show low surface energy and thus potential oil and water repellency (58). The electrospun THV fibers in the present contribution exhibited oleophilicity rather than repelling oil in addition to near and below super hydrophobicity. This shows the uniqueness and novelty of the electrospun THV fibers.

Moreover, the low oil contact angle results of electrospun fibers can be best described by the Wenzel equation regarding a liquid droplet on a rough solid surface:

$$\cos \theta_w = r \cdot \cos \theta_0 \quad (2)$$

where θ_w is the equilibrium contact angle on a rough surface, θ_0 is the intrinsic contact angle on a smooth surface, and r is the roughness factor (41). According to the Wenzel equation, in the Wenzel oleophilic state, enhancing the surface roughness can increase the surface oleophilicity. Thus, the oil droplet can penetrate into the surface cavities (51).

4 Conclusions

In this study, the potential for improving the electrospinning properties of the industrially important fluorinated terpolymer was documented. Increasing the applied voltage decreased the fiber diameter when the fibers were electrospun from THV/acetone solutions. The diameter of the fibers prepared from 15 wt% THV/acetone solutions by 16 kV (sample 2) varied between 0.87 and 3.24 μm , while the diameter range of the fibers prepared by 19 kV became narrower and was between 0.40 and 2.60 μm (sample 1). The addition of natural clay into the THV/montmorillonite solution yielded relatively thinner fibers. We suggest that hydrophilic montmorillonite functioned as a useful additive in electrospinning. The thickest fibers were obtained when ethyl acetate was used as the solvent. When the fibers were prepared from the THV/ethyl acetate solution with either the 11-gauge needle (sample 4) or the 16-gauge needle (sample 3), fibers with diameters as large as 6.33 and 5.43 μm were observed. The fibers prepared from 15 wt% THV/ethyl acetate solutions had at least twofold thicker fibers than that prepared from 15 wt% THV/acetone solutions and were approximately threefold thicker than the fibers electrospun from clay added THV/acetone solutions. The electrospun THV fibers had “near and slightly below super hydrophobic (>150°)” character, and this is independent of the

experimental conditions both in this study and the study by Ok *et al.* (20), as well as the morphology and average diameter of the fibers. The THV hydrophobicity was enhanced approximately by 40% revealed by an increase in the water contact angle from 102° on THV thin film prepared by the solution cast method to 141° on electrospun THV fiber films. Besides the hydrophobic character, the THV fibers also exhibited oleophilicity. The hydrophobicity of the electrospun THV fibers was explained by Cassie’s model, while oleophilicity of them was described by the Wenzel equation. The electrospun THV fibers might be applied as absorbent matrix systems in cleaning oil spills and in special textile coatings (59). Membranes based on electrospun THV fibers with high-temperature stability might have applications in water purification from water/oil mixtures.

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