



Electrospun PVDF-HFP/MgO Nanofiber Composites: Influence of MgO Nanoparticles Content on Nanostructure, Thermal, Mechanical, and Surface Characteristics

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Abstract. PVDF-HFP/MgO nanofiber composites have been successfully synthesized using the electrospinning process. The successful synthesis of the PVDF-HFP/MgO nanofiber composites was confirmed through XRD, FTIR, and SEM analyses. In the XRD results, distinct peaks were observed at diffraction angles of 42.80° and 62.27° in the PVDF-HFP/MgO nanofiber composites sample, corresponding to the diffraction angles of the MgO nanoparticles. The FTIR results exhibited an absorption band at a wavenumber of 667 cm^{-1} , indicating the stretching vibration of Mg-O bonds. The morphology of pure PVDF-HFP nanofibers consisted of straight primary fibers, which were extremely fine and continuous, showing no bead formation, although the uniformity was not consistent. With an increase in MgO content in the nanofiber composites, the diameter of the nanofibers decreased. TGA demonstrated that the addition of MgO increased the degradation temperature of the nanofibers. However, the incorporation of nano MgO into the nanofibers led to a decrease in their tensile strength and contact angle with water. The pure PVDF-HFP nanofiber exhibited a tensile strength of $6.26 \pm 0.25\text{ MPa}$. In comparison, the PVDF-HFP/MgO nanofiber composites at concentrations of 10%, 20%, and 30% displayed respective tensile strength values of 4.59 ± 0.43 , 3.07 ± 0.14 , and $1.32 \pm 0.04\text{ MPa}$. The pure PVDF-HFP nanofiber displayed hydrophobic characteristics with a water contact angle of $134.3^\circ (\pm 2.89)$. The introduction of MgO nanoparticles decreased the contact angle value, causing water droplets to wet the membrane more quickly. These findings collectively indicate that the presence of MgO in the nanofiber composites allows for control and adjustment of their nanostructure, thermal behavior, mechanical properties, and surface characteristics. These features lay the groundwork for potential applications of PVDF-HFP/MgO nanofiber composites. One noteworthy application suggested by the observed characteristics is the utilization

of these composites as adsorbents for pollutants in both liquid and gas environments.

Keywords: PVDF-HFP/MgO, electrospinning, nanofiber composites, characteristic.

1 Introduction

In recent years, the field of nanomaterials has witnessed remarkable advancements, offering unprecedented opportunities to engineer materials with tailored properties for a wide range of applications [1], [2]. One such area of interest lies in the development of composite materials, where the integration of nanoparticles into polymer matrices can lead to enhanced mechanical, thermal, and surface characteristics. Electrospinning, a versatile and efficient technique, has gained significant attention for fabricating nanofiber composites with precise control over fiber morphology and nanoparticle dispersion [3], [4].

Polymer nanofiber composites have exhibited exceptional potential due to their remarkable combination of properties derived from both the polymer matrix and the incorporated nanoparticles. Among the polymers employed, poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) stands out as an important candidate due to its outstanding piezoelectricity, thermal stability, and chemical resistance [5], [6], [7]. The integration of PVDF-HFP with inorganic nanoparticles, such as magnesium oxide (MgO), can impart synergistic effects, leading to improved overall performance.

MgO nanoparticles are particularly appealing due to their unique properties, including high thermal conductivity, electrical insulating capability, and exceptional mechanical strength. These characteristics make MgO a promising candidate for reinforcing polymer matrices, with potential applications in various fields [8], [9], [10].

The tuning of the mechanical, thermal, and surface properties of polymer nanocomposites often hinges on the content of the incorporated nanoparticles. The interaction between the polymer matrix and nanoparticles is strongly influenced by the loading concentration, leading to modifications in material behavior [11], [12]. In the case of electrospun nanofiber composites, the surface characteristics play a crucial role in applications where interfacial interactions dictate performance, such as in sensor technologies or membrane separations [13].

This study aims to explore the influence of MgO nanoparticle content on the thermal, mechanical, and surface properties of electrospun PVDF-HFP/MgO nanofiber composites. By systematically varying the loading concentration of MgO nanoparticles, a comprehensive understanding of the structure-property relationships can be attained. The investigation into the interplay between nanoparticle content and resulting properties will provide valuable insights for designing nanofiber composites tailored to specific applications.

The integration of MgO nanoparticles into electrospun PVDF-HFP nanofibers presents a promising avenue for achieving enhanced material properties. This study endeavors to shed light on the intricate interdependencies between nanoparticle loading, thermal behavior, mechanical performance, and surface characteristics. The findings

from this research could pave the way for the development of advanced nanofiber composites with multifaceted applications across diverse technological domains.

2 Methodology

2.1 Materials

The materials used are polyvinylidene fluoride co-hexafluoro propylene (PVDF co-HFP, Arkema Kynar Flex 2801-00), N, N-Dimethylacetamide (DMAc), ethanol, sodium hydroxide (NaOH), and disodium hydrogen arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Merck. Deionized (DI) water was used during this study. Seawater bitterns (SWBs) were collected from Madura, Indonesia.

2.2 Synthesis of MgO nanoparticles

Two moles of NaOH were gradually added dropwise into 1 mole of SWBs at a flow rate of 11 mL min^{-1} and agitated using a magnetic stirrer for 30 minutes at room temperature. Subsequently, the mixture underwent centrifugation at 3000 rpm for 15 minutes. The solid phase was subjected to two rounds of washing with ethanol and hot water at $80 \text{ }^\circ\text{C}$ to eliminate impurities, followed by drying at $60 \text{ }^\circ\text{C}$ overnight. The resulting products, identified as $\text{Mg}(\text{OH})_2$, were subjected to calcination to generate MgO at $400 \text{ }^\circ\text{C}$ for a duration of five hours, with the temperature gradually increasing at a rate of $2 \text{ }^\circ\text{C per minute}$.

2.3 Synthesis of PVDF-HFP/MgO nanofiber composites

A 24% (w/v) solution of PVDF-HFP copolymer was dissolved in 10 mL of DMAc and agitated using a magnetic stirrer for a duration of five hours. Subsequently, synthesized MgO nanoparticles were introduced, with varying weights (w/w) relative to the weight of the PVDF-HFP copolymer, into the copolymer solution. The mixture was then stirred for approximately 12 hours. The specific composition of the samples is detailed in Table 1. The resulting solution was loaded into a syringe and processed using an electrospinning apparatus at a flow rate of $16.67 \text{ } \mu\text{L min}^{-1}$. The device maintained 17 cm between the nozzle and the collector, with an applied voltage of 21 kV. The nanofibers were collected onto aluminum foil.

Table 1. Composition of PVDF-HFP nanofiber and PVDF-HFP/MgO nanofiber composites.

Sample type	PVDF-HFP copolymer (% w/v)	MgO nanoparticles (% w/w)
PVDF-HFP	24	0
PVDF-HFP/MgO 10%	24	10
PVDF-HFP/MgO 20%	24	20
PVDF-HFP/MgO 30%	24	30

2.4 Characterization

The thermal properties of the materials were investigated using Thermogravimetric Analysis (TGA) with a 209 F1 Libra instrument from Netzsch, Germany. The analysis was conducted under inert conditions using a nitrogen gas flow rate of 20 mL min⁻¹. The temperature range for the operation was set between 25 °C and 700 °C, with a heating rate of 10 °C min⁻¹. The mechanical properties were examined by measuring the tensile strength of the material using a Tensilon Universal Testing Machine (Orientec UCT-5T). The water contact angle was evaluated by the drop shape analysis (DSA) method and calculated by the equation:

$$\theta = 2 \tan^{-1} \left(\frac{h}{r} \right) \quad (1)$$

Additionally, spreading time observation was conducted by measuring the water contact angle on the material at regular intervals until the contact angle reached zero.

3 Result and Discussion

3.1 Thermal Properties Analysis

Thermogravimetric Analysis (TGA) characterization was conducted under inert conditions to determine the thermal stability and degradation pattern of the nanofibers. The testing conditions were performed within a temperature range of 25-700 °C with a heating rate of 10 °C/minute. Fig. 1 shows the TGA curve, illustrating the percentage of mass loss at specific temperatures. From the TGA curve, it can be observed that the nanofiber decomposition occurs in three stages. The decomposition of PVDF-HFP in the nanofiber depends on heating conditions, including heating rate, temperature, and atmosphere.

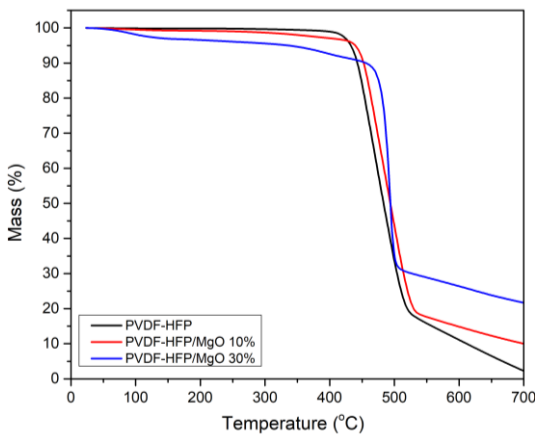


Fig. 1. Thermograms for pure PVDF-HFP nanofiber and PVDF-HFP/MgO nanofiber composites.

Table 2 provides a summary of the nanofiber's decomposition stages, consisting of three phases. In the first phase, the nanofiber experiences a mass loss of around 10% at a temperature of approximately 450 °C. This corresponds to the loss of fluoride groups and hexafluoropropylene, resulting in the evolution of volatile gases such as HF (hydrofluoric acid) and HFP (hexafluoropropylene). The second phase occurs in the temperature range of 450-520 °C, with the highest percentage of mass loss. During this phase, polymer chain degradation occurs, leading to polymer bond cleavage and the release of small molecules such as hydrocarbons [14], [15]. The final stage of the nanofiber decomposition process occurs in the temperature range of 520-700 °C, forming residue ash composed of elements remaining after the decomposition of PVDF-HFP, such as carbon and additives (in this case, MgO), or impurities in the sample [16].

Table 2. Summary of TGA results of pure PVDF-HFP nanofiber and PVDF-HFP/MgO nanofiber composites.

Sample	Stage	Temperature Range	Mass Change (%)	Residual Mass (%)
PVDF-HFP	1	23.4-442.4	-9.77	
	2	442.4-519.4	-70.07	2.31
	3	519.4-699.4	-17.85	
PVDF-HFP/MgO 10%	1	24.8-451.8	-9.64	
	2	451.8-525.8	-68.68	10.07
	3	525.8-698.8	-11.61	
PVDF-HFP/MgO 30%	1	23.6-453.6	-9.82	
	2	453.6-511.6	-59.13	21.74
	3	511.6-698.6	-9.31	

3.2 Mechanical Properties Analysis

The tensile strength test results in Fig. 2 demonstrate that the pure PVDF-HFP nanofiber has a strength value of 6.26 ± 0.25 MPa. Meanwhile, for the PVDF-HFP/MgO nanofiber composites at 10%, 20%, and 30% concentrations, their respective strength values are 4.59 ± 0.43 , 3.07 ± 0.14 , and 1.32 ± 0.04 MPa. It can be observed that the addition of MgO nanoparticles to the nanofibers leads to a reduction in tensile strength. The low compatibility between the MgO nanoparticles and PVDF-HFP nanofibers results in a rough and uneven nanofiber surface [17], contributing to the decrease in the composite nanofiber's tensile strength. Additionally, the stiffness of the composite nanofibers also increases compared to pure PVDF-HFP nanofibers due to the incorporation of high-crystallinity MgO nanoparticles [18], [19]. The decrease in tensile strength of the composite nanofibers compared to the pure PVDF-HFP nanofibers may also be attributed to the entrapment of MgO nanoparticles within the fibers.

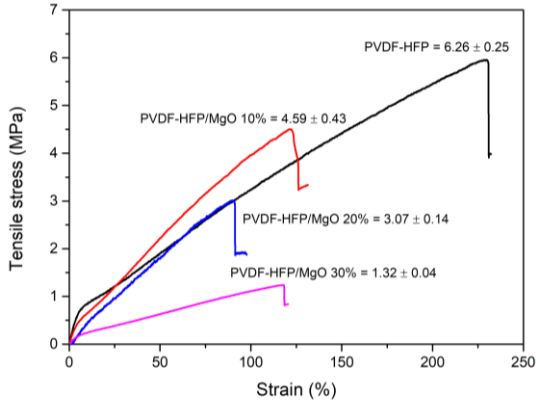


Fig. 2. Tensile stress-strain curves of PVDF-HFP, PVDF-HFP/MgO 10%, PVDF-HFP/MgO 20%, and PVDF-HFP/MgO 30%.

3.3 Hydrophobicity Analysis

The hydrophobicity of nanofibers and nanofiber composites is determined by measuring their contact angle with water. Hydrophobicity can influence the adsorption performance of an adsorbent [20]. The contact angle is the angle formed by the inclination of a droplet of liquid placed on the surface of a membrane. The contact angle is measured using the Drop Shape Analysis (DSA) method. A small contact angle ($< 90^\circ$) indicates a high level of wetting (the membrane is hydrophilic), while a large contact angle ($> 90^\circ$) indicates a low level of wetting (the membrane is hydrophobic).

Fig. 3 indicates that the pure PVDF-HFP nanofiber is hydrophobic with a contact angle value of $134.3^\circ (\pm 2.89)$. The incorporation of MgO NPs into the nanofiber reduces the contact angle value. The more MgO NPs are added, the smaller the contact angle value becomes, although not significantly so.

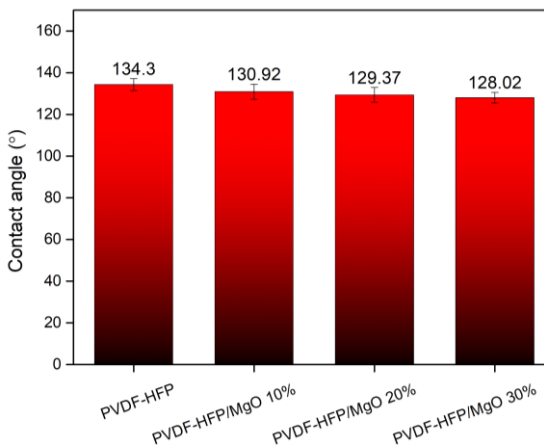


Fig. 3. Water contact angle on pure PVDF-HFP nanofiber and PVDF-HFP/MgO nanofiber composites.

Further characterization regarding the nanofiber hydrophobicity was conducted through spreading time analysis. Measurements were performed to determine the time required for a liquid to completely wet the membrane. In Figure 4, it is shown that the addition of MgO NPs accelerates the time required for a water droplet to wet the membrane. In pure PVDF-HFP nanofibers, a water droplet takes up to 190 minutes to fully wet the membrane (totally wetting). Meanwhile, the PVDF-HFP nanofiber composites with 10%, 20%, and 30% (w/w) MgO, require 180, 150, and 140 minutes respectively to achieve full wetting.

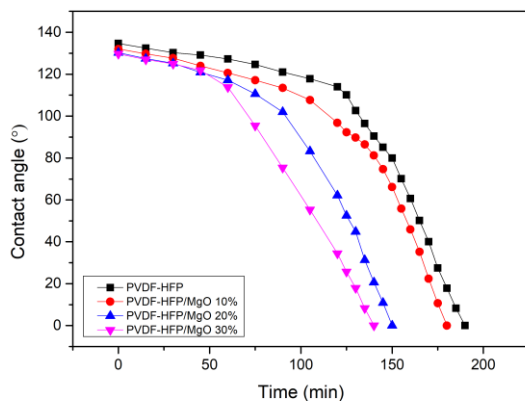


Fig. 4. Water spreading time on pure PVDF-HFP nanofiber and PVDF-HFP/MgO nanofiber composites.

4 Conclusion

This The nanofiber composites PVDF-HFP/MgO have been successfully synthesized. The addition of MgO nanoparticles to the PVDF-HFP nanofiber reduces its tensile strength, decreases its contact angle, and accelerates the spreading time of water on the nanofiber. These characteristics can serve as a basis for further research, especially when considering potential applications of the PVDF-HFP/MgO composite nanofibers. One of the potential applications suggested by the characteristics observed in this study is the use of the PVDF-HFP/MgO composite nanofibers as adsorbents for pollutants in both liquid and gas media.

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