Investigation of the Effect of Different Reducing Agents Used in the Production of Nanofibers with Graphene Oxide on Water Contact Angle and Determination of its Application Area

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Studies investigating the functional properties of nanofiber structures are noteworthy due to the multidisciplinary nature of the subject. Graphene oxide-containing polymer solutions used to obtain nanofiber structures, which are part of a growing group of studies due to their numerous and diverse applications, are highly varied. The literature shows that different reducing agents are used in the preparation of polymer solutions and the reduction of graphene oxide. By choosing natural reducing agents, our study will serve as an example of an environmentally friendly approach and contribute to a sustainable environment. Wettability is a property that can be defined as the coverage of a surface with water or another liquid. The wettability property is determined by measuring the contact angle of the droplet on the structure. If the measured contact angle is less than 90 degrees, the surface is wettable; if it is greater than 90 degrees, the surface is non-wettable [1]. This surface condition is a characteristic that will determine the product's area of application. This study aims to investigate how the water contact angles of nanofiber structures produced under the same conditions will change with the variation of reducing agents and to determine their areas of application.

In this study, polyvinylidene fluoride (PVDF) and graphene oxide (GO)-reinforced PVDF nanofibers were formed on polyester spunbond nonwoven fabric coated with an aqueous dispersion of graphene oxide using the dip-coating method and the electrospinning method. Graphene oxide dip-coated spunbond nonwoven fabric was used as the substrate fabric.

Subsequently, PVDF and GO-modified PVDF nanofiber surfaces were formed on GO-coated and reduced nonwoven fabrics using the electrospinning method. Polymer solutions were prepared as pure PVDF containing 0.5% by weight, 1% by weight, and 2% by weight GO. A chemical reduction process was applied to nonwoven spunbond fabric coated with graphene oxide and containing GO-doped PVDF nanofibers using vitamin C and rosehip extract powder. Water contact angle results were evaluated to determine functional properties. Vitamin C and rosehip were identified as two natural reducing agents for the reduction of graphene oxide. The use of nature- and human-friendly reducing agents is consistent with the principle of sustainability.

Keywords: Graphene oxide, nanofiber, electrospinning, natural reduction, water contact angle

1. INTRODUCTION

Nanofibers offer significant advantages such as high surface area to mass ratio, low density, flexibility in surface properties, excellent mechanical properties, high pore volume, and low pore size [2,3]. In our study, the electrospinning method, one of the most commonly used methods for nanofiber production, was preferred. Using the electrospinning method, electrically charged polymer jets elongate under a high electric field and accumulate on the collector surface in the form of ultra-fine solid fibers as the solvent evaporates [4]. Graphite synthesis, on the other hand, involves oxidation and reduction processes that result in graphene formation.

Graphene and its derivatives have a wide range of applications, from nanoelectronics to biomedicine. In textiles, they are used for flexible wearable electronics, information transfer, and shock response [5-6]. Graphene-based materials are preferred in sensors due to their flexibility and good electrical conductivity [7].

Many researchers have investigated graphene oxide coatings on textile surfaces. Yapıcı and Alkhıdır [8] coated nylon fabric with GO using dip coating and reduced it with hydroiodic acid, then investigated the use of the resulting reduced GO/nylon fabric as an ECG sensor. Several studies have investigated the effects of GO-coated fabrics on electrical surface resistance [9–11]. Şimşek [12] investigated the production of PVDF nanofibers using the electrospinning method and their piezoelectric properties. Numerous studies have been conducted in the literature on the coating of textile surfaces with GO. In most of these studies, woven or knitted fabrics were coated with GO using various methods, then GO was reduced and its properties were examined.

Although the electrospinning method has been used in most studies involving PVDF, to date, no study has been conducted using both GO coating and GO-modified PVDF polymer solution on a nonwoven fabric.

Various methods, primarily chemical and thermal, are used for the reduction of graphene oxide. The most commonly studied chemical reducing agents include hydrazine hydrate, L-ascorbic acid (vitamin C), sodium borohydride ($NaBH_4$), and similar reducing agents, as well as reducing gases [13]. Each method increases the C/O ratio by reducing the oxygen groups on the GO surface, making the surface more hydrophobic. For example, hydrazine reduction converts GO almost completely to rGO, resulting in a very high water contact angle [13]. Thermal reduction, on the other hand, purifies GO at high temperatures. Nanofibers heated to the extent permitted by the suitable polymer matrix (>200–300 °C) also lose oxygen to a large extent. The rGO surfaces obtained after thermal treatment also acquire a hydrophobic character [14].

When examining the contact angle changes observed after GO reduction in the literature;

- GO (unreduced): Typically $\theta \approx 26°–50°$ (hydrophilic)[15].
- rGO (hydrazine/thermal reduction): High θ (hydrophobic or superhydrophobic). For example, Adotey et al. reported a water contact angle >150° for rGO obtained by hydrazine chemical reduction, observing very strong hydrophobicity [16]. In another study, $\theta \approx 139°$ was measured for rGO integrated into a PVDF nanofiber membrane [17].
- rGO ($NaBH_4$ reduction): Typically $\theta > 90°$ (hydrophobic). For example, in one study, the contact angle of a $NaBH_4$-reduced GO/PCL film was ~89.8° [18]. This indicates that GO exhibits a hydrophobic structure after $NaBH_4$ reduction.
- rGO (L-ascorbic acid reduction): Again $\theta > 90°$ (hydrophobic). rGO coatings obtained by L-ascorbic acid reduction can exhibit superhydrophobic properties (θ ~120–150° in places) [19].
- rGO (other reduction agents): Generally, θ increases as hydrophilic groups decrease; for example, reduction with $Na_2S_2O_4$ also provides high θ [20].

Table 1. Application areas of reduction methods in the literature according to the feature obtained

Reduction Method	**Approximate Contact Angle (WCA)**	**Hydrophilic/Hydrophobic Properties**	**Application Areas**
Pure GO (unreduced)	~26–50° (low)	Hydrophilic	Tissue engineering, water retention, nanocomposites [15]
Hydrazine (chemical)	~150° (very high)	Superhydrophobic	Protective coatings, oil-water separation, energy applications [16]
L-Ascorbic Acid (chemical)	>90° (high)	Hydrophobic	Filter/membrane, composite materials [19]
$NaBH_4$ (chemical)	~90° (high)	Hydrophobic	Composite fibers, electron additives [18]
Thermal Reduction	>90° (high, ~139°)	Hydrophobic	Electronics/energy (flexible electrodes), water treatment membranes [17]

The literature shows that many different reducing agents are used in the reduction of GO. In this study, the production of GO-containing PVDF nanofibers on GO-coated polyester nonwoven fabric by electrospinning was investigated, and the effect of the different reducing agents used on the functional properties of the resulting fabrics, specifically the water contact angle, was examined. The aim was to propose new applications.

The fact that the selected reducing agents are environmentally and human-friendly also contributes to this study's sustainability.

This research has the potential to add a new dimension to the development of smart textiles and provide innovative solutions for technological applications.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals were of analytical reagent grade and were used without further purification. Graphite sheets, acetone, dimethylformamide (DMF), and vitamin C (L-ascorbic acid) were purchased from Sigma Aldrich. Sulfuric acid (H_2SO_4, 95-98%), potassium permanganate ($KMnO_4$), and ethanol were purchased from Isolab. Hydrogen peroxide (H_2O_2, 35%), phosphoric acid (H_3PO_4), and hydrochloric acid (HCl, 37%) were purchased from Merck. Water-soluble rosehip extract powder (Rosa canina) was purchased from Naturalya Kimya (Turkey). Distilled water was used throughout the experiments. Polyester spunbonded nonwoven fabric with a base weight of 25 g/m² was used as the substrate fabric. PVDF (Mw = 244000, Solef® 1000 series) was supplied by Solvay.

2.2. Synthesis of Graphene

Graphene oxide was synthesized from flake graphite using the Hummer method, as modified by [21]. Briefly, graphite flakes (3 g) and $KMnO_4$ were mixed with a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) (18 g). The reaction was then heated to 50°C and stirred for 12 hours. The reaction was then cooled to room temperature and poured onto ice (400 mL) with 35% H_2O_2 (6 mL). The resulting suspension was washed by repeated centrifugation (30 minutes at 8000 rpm each) first with 400 mL of 1 M HCl and 200 mL of ethanol (x2), then with distilled water until a pH of 4-5 was achieved. The resulting solid product was dried overnight in an oven at 60°C.

2.3. Electrospinning

Graphene oxide nanolayers were synthesized from graphite using the modified Hummer's method. A 2 g/L GO aqueous dispersion was prepared using the obtained graphene oxide. The obtained 100% polyester nonwoven fabrics were coated by immersion with the prepared GO aqueous dispersion and prepared for the electrospinning process. The bath ratio for dip coating was determined as 1:20. For the production of GO-doped PVDF nanofibers, the electrospinning parameters were set as a collector distance of 12 cm, a collector rotation speed of 200 rpm, a feed rate of 2 mL/h, and an applied voltage of 27 kV. For the electrospinning process, the pure polymer solution was prepared at 50 °C using a magnetic stirrer at a 3:2 ratio (DMF/Acetone) with 10% PVDF by weight. To prepare the GO-modified PVDF solution, GO ratios were determined and prepared at 0.5% by weight, 1% by weight, and 2% by weight.

The environmentally friendly reducing agents determined for the reduction process of the nanofiber structure obtained on nonwoven fabric are Vitamin C (L-ascorbic acid) and rosehip powder extract. A 0.2 M aqueous Vitamin C solution was prepared for the reduction process with Vitamin C. For the reduction process with rosehip extract, a 0.5% w/w Vitamin C and 10% w/w aqueous rosehip extract solution was prepared. After the electrospinning process, the samples were reduced with Vitamin C at 95°C for 90 minutes and with rosehip extract solution for 5 hours. At 95°C. After the reduction process, the samples were washed with distilled water using a stepwise washing method and dried in an oven for 60 minutes. The codes assigned to the obtained samples are shown in Table 2.

Table 2. Contents of the fabrics produced, processes applied, and codes assigned

Sample Code	**Fabric Composition and Processes Applied**
05GO	PVDF nanofiber with 0.5% GO content by weight
05RGO-R	PVDF nanofiber containing 0.5% GO by weight (reduction with rosehip)
05RGO-C	PVDF nanofiber containing 0.5% GO by weight (reduced with vitamin C)
1GO	PVDF nanofiber with 1% GO content by weight
1RGO-R	PVDF nanofiber containing 1% GO by weight

	(reduction with rosehip)
1RGO-C	PVDF nanofiber containing 1% GO by weight (reduced with vitamin C)
2GO	PVDF nanofiber with 2% GO content by weight
2RGO-R	PVDF nanofiber with 2% GO content by weight (reduction with rosehip)
2RGO-C	PVDF nanofiber containing 2% GO by weight (reduced with vitamin C)
NW	Nonwoven Fabric

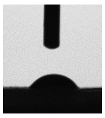
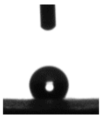
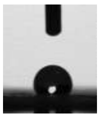
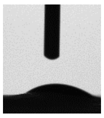
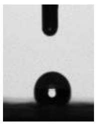
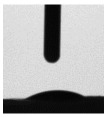
2.4. Characterization

Since the aim of the study was to investigate the effects of the differences in the reducing agents on the water contact angle, the water contact angle measurements of the nonwoven and nanofiber samples were measured using a contact angle meter (CAM 100, KSV Instruments).

3. RESULTS AND DISCUSSION

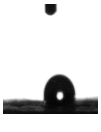
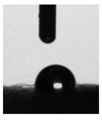
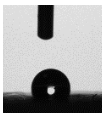
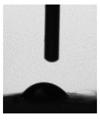
Water contact angle measurements were performed separately for all samples and are presented in Tables 3 and 4 for nanofibers and nonwoven fabrics, respectively, along with the corresponding droplet images. Table 3 shows that pure PVDF nanofiber is hydrophobic, as it has a water contact angle higher than 90°. Adding a small amount of GO to the nanofiber structure causes a slight increase in the water contact angle. Increasing the GO concentration in the PVDF polymer matrix has no effect on the water contact angle of the nanofibers. The highest water contact angle of 129.8° was obtained in the GO-modified PVDF nanofiber containing 0.5% GO by weight. Although the water contact angle values of the nanofibers tend to decrease with increasing GO content, the obtained values still indicate hydrophobicity. The reduction of GO-modified PVDF nanofibers with Vitamin C (RGO-C) preserved their hydrophobicity. Conversely, the water contact angle of RGO-R samples decreased significantly, reaching values below 90°, indicating hydrophilicity.

Table 3. Water contact angle measurement results and droplet images of electrospun nanofibers.

Water contact angle (°) and droplet images									
PVDF	**0.5%**			**1%**			**2%**		
	GO	**RGO-C**	**RGO-R**	**GO**	**RGO-C**	**RGO-R**	**GO**	**RGO-C**	**RGO-R**
121.1 	129.8 	124.2 	61.2 	128.8 	124.5 	28.2 	124.1 	119.3 	26.8 

The water contact angle results and corresponding droplet images of GO and RGO-coated nonwoven fabric samples are presented in Table 3. Since all nonwoven fabrics were coated in the same manner, one measurement was taken as a reference measurement for all GO-coated nonwoven fabrics. The water contact angle of the polyester nonwoven fabric was measured as 108.6°. When examining the water contact angle values of nonwoven surfaces, it can be seen that the nonwoven fabric coated with GO can be considered hydrophobic because its water contact angle is 90°. However, a slight decrease was obtained in the water contact angle of the nonwoven fabric coated with GO compared to the plain nonwoven fabric. After the reduction with vitamin C, the water contact angle increased to 94°. However, the water contact angle of the sample reduced using rosehip extract powder decreased significantly, and the surface of the sample became hydrophilic.

Table 4. Water contact angle results (°) and droplet images of GO-coated and RGO-coated nonwoven fabrics.

Water contact angle (°) and droplet images			
NW	**NW-GO**	**NW-RGO-C**	**NW-RGO-R**
108.6 	90.6 	94.1 	48.1 

The hydrophilic nature of graphene oxide and the hydrophobic character of reduced graphene oxide are key properties that guide the application areas of nanofiber materials. Hydrophilic GO-layered nanofiber matrices are advantageous in biomedical applications because GO increases water retention capacity in tissue and thus supports cell adhesion [13]. Furthermore, membrane surfaces with high hydrophilicity interact rapidly with water, and this interaction enhances the permeation performance of water filtration membranes [22-23].

However, hydrophobic reduced graphene oxide nanofiber surfaces obtained after reduction are preferred in oil-water separation, water-repellent coatings, and water purification membranes. Superhydrophobic rGO coatings are effective in trapping oil liquids and separating them from water. The electro-spun rGO/PVDF-HFP membranes (~139° WCA) developed by Chen et al. are important for seawater distillation and wastewater treatment [17]. Furthermore, hydrophobic-surfaced nanofibers are also used in anti-corrosion coatings and energy devices requiring corrosion resistance.

Looking at the reduction method, contact angle change, and application summary provided in Table 1, hydrophilic GO nanocomposites are generally directed toward biomedical and water purification applications, while hydrophobic rGO nanofibers are directed toward oil separation, water repellency, coatings, sensors, and energy applications [24-25]. In summary, the choice of application often depends on whether the surface is hydrophilic or hydrophobic: For example, GO-enriched electrofiber membranes provide biocompatibility and water permeability, while hydrophobic fibers containing reduced GO are effective in water-resistant filtration and protective coating applications.

In this study, the surface wettability behaviors of graphene oxide (GO)-doped PVDF nanofiber structures produced on polyester nonwoven fabric surfaces via the electrospinning method and subsequently reduced using different environmentally friendly reducing agents were comparatively investigated. The results obtained revealed that the nanofiber structures exhibited distinctly different surface characteristics depending not only on the GO content but also on the chemical nature of the reducing agent used.

Water contact angle measurements showed that PVDF nanofibers produced at low GO ratios (0.5%) exhibited higher hydrophobicity, and this effect decreased to a limited extent as the GO ratio increased. However, the results obtained after reduction revealed that the surface character was primarily determined by the reducing agent. It was determined that GO-containing PVDF nanofibers reduced with vitamin C largely retained their hydrophobic properties, whereas nanofibers reduced with rosehip extract acquired a distinctly hydrophilic character.

This situation constitutes the fundamental aspect that distinguishes this work from similar GO/PVDF systems in the literature. It has been demonstrated that under the same polymer matrix, the same GO ratio, and the same production conditions, only by changing the reducing agent, the surface can exhibit hydrophilic or hydrophobic behavior. Thus, the reducing agent has evolved from being a secondary process determining surface functionality to becoming a design parameter that directly defines the application area.

In light of the data obtained, it is considered that nanofiber structures reduced with rosehip extract and gaining hydrophilic properties offer potential applications in areas such as flow-regulating surfaces where controlled liquid spreading, rapid wetting, and surface interaction are important, technical textiles requiring moisture management, and smart textile-based sensing surfaces. In contrast, it is thought that nanofiber structures reduced with vitamin C and retaining their hydrophobic character are suitable for passive barrier surfaces where liquid retention is undesirable and surface stability and contact angle are critical, as well as for interlayers in multilayer membrane systems or surface energy-controlled textile composites.

In this respect, the study demonstrates that the reduction agent is not merely an environmental preference, but also an effective design tool that determines the functional behavior and potential application areas of nanofiber surfaces. The ability to achieve different surface functions within the same nanofiber system using eco-friendly reduction agents contributes significantly to the development of sustainable and multifunctional textile surfaces.

REFERENCES

[1] Burton, Z., & Bhushan, B. (2006). Surface characterization and wettability analysis by ultramicroscopy. Ultramicroscopy, 106 (8–9), 709–719.

[2] Li, D., & Xia, Y. (2004). Electrospinning of nanofibers: Reinventing the wheel? Advanced Materials, 16(14), 1151–1170.

[3] Greiner, A., & Wendorff, J. H. (2007). Electrospinning: A fascinating method for the preparation of ultrathin fibers. Angewandte Chemie International Edition, 46(30), 5670–5703.

[4] Reneker, D. H., & Yarin, A. L. (2008). Electrospinning jets and polymer nanofibers. Polymer, 49(10), 2387–2425.

[5] Wang, D., Li, D., Zhao, M., Xu, Y., & Wei, Q. (2018). Multifunctional wearable smart device based on conductive reduced graphene oxide/polyester fabric. Applied Surface Science, 454, 218–226.

[6] Ruckdashel, R. R., Khadse, N., & Park, J. H. (2022). Smart e-textiles: Overview of components and outlook. Sensors, 22(16), 6055.

[7] = Liu, J., Bao, S., & Wang, X. (2022). Applications of graphene-based materials in sensors: A review. Micromachines, 13(2), 184.

[8] Yapici, M. K. & Alkhidir, T. E. (2017). Intelligent medical garments with graphene-functionalized smart-cloth ECG sensors. Sensors, 17(4), 875.

[9] Fugetsu, B., Sano, E., Yu, H., Mori, K., & Tanaka, T. (2010). Graphene oxide as dyestuffs for the creation of electrically conductive fabrics. Carbon, 48, 3340–3345.

[10] Jang, H.-S., Moon, M. S., & Kim, B. H. (2021). Electronic textiles fabricated with graphene oxide-coated commercial textiles. Coatings, 11(5), 489.

[11] Cao, J., & Wang, C. (2017). Multifunctional surface modification of silk fabric via graphene oxide repeatedly coating and chemical reduction method. Applied Surface Science, 405, 380–388.

[12] Şimşek, R. (2015). Polyvinylidene fluoride (PVDF) polimerinden nanolifli yüzeylerin elde edilmesi ve bu yüzeylerin enerji üretim özelliklerinin incelenmesi (Yüksek lisans tezi). Marmara Üniversitesi, Fen Bilimleri Enstitüsü, İstanbul, Türkiye.

[13] Dreyer, D. R., Park, S., Bielawski, C. W., & Ruoff, R. S. (2010). The chemistry of graphene oxide. Chemical Society Reviews, 39(1), 228–240.

[14] Pei, S., & Cheng, H. M. (2012). The reduction of graphene oxide. Carbon, 50(9), 3210–3228.

[15] Liu, S., Zeng, T. H., Hofmann, M., Burcombe, E., Wei, J., Jiang, R., Kong, J., Chen, Y., & Chen, Y. (2011) Antibacterial activity of graphite, graphite oxide, graphene oxide, and reduced graphene oxide: Membrane and oxidative stress.

[16] Adotey, E., Kurbanova, A., Ospanova, A., Ardakkyzy, A., Toktarbay, Z., Kydyrbay, N., Zhazitov, M., Nuraje, N., & Toktarbaiuly, O. (2025). Development of superhydrophobic reduced graphene oxide (rGO) for potential applications in advanced materials. Nanomaterials, 15(5), 363.

[17] Chen, T., Soroush, A., & Rahaman, M. S. (2018). Highly hydrophobic electrospun reduced graphene oxide/poly(vinylidene fluoride-co-hexafluoropropylene) membranes for use in membrane distillation. Industrial & Engineering Chemistry Research, 57(43), 14535–14543.

[18] Zhang, H., Zhang, X., Zhang, Y., & Wang, W. (2015). Preparation and characterization of reduced graphene oxide/polycaprolactone (rGO/PCL) nanocomposites. Journal of Materials Science: Materials in Electronics, 26, 7320–7327.

[19] Li, X., Zhang, G., Bai, X., Sun, X., Wang, X., Wang, E., & Dai, H. (2008). Chemically derived, ultrasmooth graphene nanoribbon films for flexible electronics. Journal of the American Chemical Society, 130(51), 16739–16744

[20] Chudziak, T., Montes-García, V., Czepa, W., Pakulski, D., Valentini, C., Bielejewski, M., … & Samorì, P. (2023). A comparative investigation of chemical reduction of graphene oxide for electrical engineering applications. Nanoscale.

[21] Gültekin N., Usta İ., Yalçin B., Green Reduction of Graphene Oxide Coated Polyamide Fabric Using Carob Extract, AATCC Journal of Research, 2020, 7(6):33-40.

[22] Zhang, Y., Li, X., Wang, H., & Liu, J. (2025). Enhanced water flux in nanocomposite membranes via surface hydrophilicity modification. Journal of Polymer Research, 32(5), 123 135.

[23] Kumar, S., Singh, R., Patel, A., & Verma, P. (2023). Graphene oxide reinforced hydrogel membranes for enhanced water filtration performance. Membranes, 13(7), 456.

[24] Asghar, F. (2022). Fabrication and prospective applications of graphene oxide and reduced graphene oxide nanocomposites: A review. RSC Advances.

[25] Huang, Y. (2025). Application of graphene oxide-assisted membranes in water treatment. International Journal of Low-Carbon Technologies.

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