

# THE EFFECT OF DISPERSION PREPARATION TYPE AND LAST COAGULATION BATH ON GRAPHENE OXIDE FIBERS PRODUCED BY WET SPINNING TECHNIQUE

## DİSPERSİYON HAZIRLAMA TİPİ VE SON KOAGÜLASYON BANYOSUNUN YAŞ ÇEKİM METODU İLE ÜRETİLEN GRAFEN OKSİT LİFLERE ETKİSİ

Nuray UÇAR<sup>1</sup>, Gökçen GÖKÇELİ<sup>2</sup>, Nilgün KARATEPE<sup>3</sup>, Ayşen ÖNEN<sup>4</sup>

<sup>1</sup>*Istanbul Technical University, Textile Engineering Department, Istanbul, Turkey*

<sup>2</sup>*Istanbul Technical University, Nano Science and Nano Engineering Department, Istanbul,*

<sup>3</sup>*Istanbul Technical University, Institute of Energy, Renewable Energy Division, Istanbul*

<sup>4</sup>*Istanbul Technical University, Department of Chemistry, Istanbul, Turkey*

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### ABSTRACT

Graphene oxide (GO) fiber is a promising material because of its unique properties such as high electrical conductivity, good thermal and mechanical properties and scalable production. It can have widespread usage area such as energy storage devices, sensors, catalysis, biological applications. As seen from literatures, the studies on GO fiber produced by wet spinning technique are very limited because only a few years ago, the studies on this area were started. In this study, different dispersion rate, different dispersion time and different content of acetone in the last coagulation bath have been studied. Thus, for the first time, the effect of preparation method of GO dispersion and the content of highly evaporative solvent in the last coagulation bath on mechanical and electrical properties of GO fiber have been examined. It has been seen that dispersion rate has higher positive effect on mechanical properties than dispersion time. The samples lasted by %100 acetone coagulation bath have a lower mechanical property than the sample lasted by % 20/80 (distilled water/acetone). Among samples, highest mechanical properties belong to sample with coagulated by CaCl<sub>2</sub>-ethanol and dispersed for 90 minute by 15 000 rpm. Meanwhile coagulated samples with NaOH-acetone had the lowest mechanical properties. With regard to electrical conductivity, all samples are in the semi conductive range (10-4 S/cm).

**Keywords:** Graphene Oxide Fiber, Wet Spinning, Coagulation Bath, Dispersion Rate, Dispersion Time, Electrical Conductivity, Mechanical Properties, Semi Conductive, CaCl<sub>2</sub>, NaOH, Ethanol, Acetone.

### ÖZET

Grafen oksit (GO) lifi, yüksek elektrik iletkenliği, uygun termal ve mekanik özellikleri ve üretim kolaylıkları sebepleri ile oldukça ilgi çekici bir konumdadır. Enerji, sensor, katalist vb. pek çok alanda kullanım potansiyeline sahiptir. Çok yakın bir zamanda, yaş çekim metodu ile üretilen GO lifleri üzerine çalışmalar başlandıktan, oldukça kısıtlı sayıda çalışma literatürde mevcuttur. Bu çalışmada ise, farklı süre ve farklı devir/dakika 'da GO dispersiyonu hazırlanmış, son koagülasyon banyosunda ise farklı oranda aseton kullanılmıştır. Böylece, ilk defa, GO dispersiyonu hazırlama metodunun ve son koagülasyon banyosundaki aseton oranının, GO lifinin mekanik ve elektrik iletkenliği üzerine olan etkisi incelenmiştir. GO dispersiyonunun hazırlanmasında uygulanan devir/dakikanın, dispersiyon süresine kıyasla mekanik özellikler üzerine etkisinin çok daha fazla olduğu görülmüştür. Son koagülasyon banyosu %100 aseton olan numunelerin mekanik özellikleri, %80 aseton-%20 su içeren numunelere göre daha düşüktür. Numuneler arasında, en yüksek mekanik özellikler, CaCl<sub>2</sub>-etanol ile koagüle olan ve dispersiyonu 15 000 devir/dakika, 90 dakika şeklinde hazırlanan numunelerde görülmüştür. Diğer taraftan NaOH-aseton ile koagüle edilen numuneler en düşük mekanik özelliklere sahip olmuştur. Tüm numuneler elektrik iletkenliği bakımından yarı iletken malzeme grubuna girmektedir (10-4 S/cm).

**Anahtar Kelimeler:** Grafen Oksit Lifi, Yaş Çekim Metodu, Koagülasyon Banyosu, Dispersiyon Oranı, Dispersiyon Süresi, Elektrik İletkenliği, Mekanik Özellikler, Yarı İletken, CaCl<sub>2</sub>, NaOH, Etanol, Aseton.

**Corresponding Author:** Nuray Uçar, e-mail: ucarnu@itu.edu.tr

## 1. INTRODUCTION

The graphene is a very promising material because of its unique properties such as excellent mechanical strength, high electrical conductivity, good thermal stability, easy handle and scalable production (1-4). The intriguing properties of graphene cause a widespread usage in energy storage devices, sensors, catalysis, biological applications and so on (1, 5).

In recent years, several studies done by researchers focused on the production of continuous graphene oxide (GO) fiber and graphene fibers which are the reduced GO fiber. As seen from these studies, mostly wet spinning technique with coagulation bath has been used (1, 3, 4, 6-13). Some of these studies investigate the effect of different chemicals used in coagulation baths on GO fiber (1, 6, 7, 10, 11). For example; Cong *et al.* clarified the assembly mechanism of the GO sheets into macroscopic fibers in a coagulation bath which include low concentration of hexadecyltrimethyl ammonium bromide (CTAB) solution. When negatively charged GO dispersion injected into positively charged CTAB solution, firstly repulsion occurred between GO nanosheets and CTAB molecules due to the electrostatic interactions. Then, the charge neutralization made contribution to adsorption of CTAB on GO thin film. Based on increasing adsorption, the assembling process started and it was resulted with the production of neat macroscopic GO fibers by means of curling from the two edges towards the center (1). Kim *et al.*, fabricated the self-assembled GO fibers by utilizing a diamine cross-linker. The diamine molecules stabilized and fixed the orientation of GO layers as coagulation agents that linked the GO layers via ion bridges during the spinning process. Consequence of the rapid acid-base reactions between the basic amine functional groups on the diamine linker and the acidic functional groups such as in-plane hydroxyl or carboxylic groups on the GO layers, the ion bridges occurred (6). Xu *et al.*, studied with the different coagulation baths such as KOH, CuSO<sub>4</sub> and CaCl<sub>2</sub> solutions for giant graphene oxides (GGO). They compared the mechanical strength and electrical conductivity of GGO in these coagulation baths. As a result of these examinations, the fiber coagulated with CaCl<sub>2</sub> solution nearly doubled the tensile and the Young's modulus compared to KOH coagulation bath, on account of Ca<sup>2+</sup> was homogenously distributed through the whole fiber (7). Xu *et al.*, produced the Ag-doped/ hybridized graphene fibers by wet spinning technique and the fibers showed high electrical conductivity due to the metal hybrids and good mechanical strength (10). Aboutalebi *et al.* examined the electrical properties of graphene fiber yarns generated through calcium chloride (CaCl<sub>2</sub>), sodium hydroxide (NaOH) and acetone coagulation baths. Use of alkaline and divalent cation baths leads to formation of impurities and adulteration of carbon bonds that result in lower electric capacitance. Compared to CaCl<sub>2</sub> and NaOH, GO dispersions fabricated in acetone bath exhibited much better electrochemical properties due to decreasing adulteration effects of impurities (11). Xiang *et al.* examined two types of GO flakes: large flake GO (LFGO) with the average diameter of 22 μm, and small flake GO (SFGO), which is 9 μm on average in diameter. SFGO was easily dispersed in water

and formed liquid crystal phase with efficient and stable drawing, yielding highly aligned fibers, while fibers spun from LFGO showed high flexibility with unusual 100% knot efficiency (12). According to the study of Dong *et al.* after drying process, the graphene fiber maintains the length but its diameter has a considerable reduction because of the water loss compared to wet fibers. The drastic shrinkage in the diameter direction during the drying process could cause the surface tension force for self-produce orientation of graphene sheets partially. During the loss of water, the capillary force could induce the close packing of porous graphene sheets which provides densely stacked and comparatively aligned graphene sheets in the fiber structure (14).

In some studies, the reduction process was also applied to the GO fibers in order to produce graphene fiber (3, 7-9, 15, 16). For example, Chen *et al.*, realized the chemical reduction of large area graphene oxide fiber (LGO) by using hydroiodic acid (HI). They pointed out that the use of LGO contributes the enhancement in mechanical properties (3). After the reduction process, the van der Waals interaction provides the decreasing in interlayer space and the hydrogen bond between residual oxygen functional groups result in the improvement in the mechanical properties (7). Jalili *et al.*, used hydrazine as a reducing agent and they observed increase in the electrical conductivity but the mechanical properties were found poorer compared to the GO fiber. This decrease in mechanical properties after hydrazine vapor treatment was attributed to the considerable expansion of the GO fiber diameter (8). Besides, Jang *et al.*, applied thermal reducing to the chemically reduced graphene oxide nanoribbon fibers (RGONRs). They annealed the RGONRs at different temperatures under Argon flow. A slight decrease in the fiber diameter was observed and it was attributed to desorption of oxygen-containing functional groups. Additional thermal annealing process resulted in the increase of electrical conductivity (15). Zhao *et al.* developed a straightforward approach for continuously production of morphology-controlled graphene based hollow fibers and applied thermal or chemical reduction to them in order to reach desirable functionalities and morphologies for various applications. They covered the graphene oxide hollow fiber (GOHF) with SiO<sub>2</sub> nanospheres (16).

Li *et al.* examined the effect of surface tension on film-to-fiber transformation process. In this study, graphene film which is produced by chemical vapor deposition technique is drawn out from ethanol bath and it shrinks into a fiberlike structure with the evaporation of ethanol. They demonstrated that, higher solvent evaporation rate creates the surface tension and ethanol solution diluted by water reduces the shrinkage (17).

As seen from literatures, since 2011 there are very limited studies (13) done on continuous Graphene Oxide (GO) fiber produced by wet spinning technique. Most of them focused on the effect of coagulation bath and reduction method on final properties of fiber. However, there are no studies done to search the effect of preparation methods of GO dispersion on the mechanical and electrical properties of continuous GO fiber, although homogenous dispersion GO

flakes and separation of each flake of GO during preparation of the GO dispersion can have very significant effect on properties of GO fiber. In this study, for the first time, the effect of dispersion time and revolution per minute during preparation of GO dispersion on mechanical, electrical properties of GO fiber have been analyzed. Besides, one other study was also carried out in order to analyze the effect of different content of solvent at the last coagulation bath on properties of GO fiber. Thus, some original results which make a contribution to limited number of literatures have been pointed out.

## 2. MATERIALS AND METHODS

**Materials:** Natural graphite flake (GRAFEN-Gr, thickness: 20 $\mu$ m, diameter: 300 $\mu$ m) was used to prepare GO fiber.  $KMnO_4$  (Merck, M: 158.03 g/mol),  $H_2SO_4$  (Merck, M: 98.08 g/mol),  $NaNO_3$  (ZAG, M: 84.99 g/mol),  $H_2O_2$  (Carlo Erba, M: 34,015 g/mol), HCl (%37, Merck) have been used during preparation graphene oxide (GO) dispersion by Hummers method.  $CaCl_2$  (Granular Calcium Chloride, Merck, M: 110.98 g/mol), Ethanol (Merck, M: 46.07 g/mol) and distilled water have been used in the coagulation bath for the study done to examine the effect of dispersion technique on GO fiber's properties. NaOH (Granular, Merck, M:39,99711 g/mol) Acetone (ZAG, M: 58.08 g/mol) and distilled water have been used in the coagulation bath for the study done to examine the effect of last coagulation bath containing solvent with high evaporation rate.

**Production of Graphene Oxide and GO Fibers:** Natural flake graphite has been used to produce graphene oxide (GO) by the Hummers method (18). When the production of GO by Hummers method was completed, the GO solution washed several times by centrifuge device (Nüve, NF800R). GO solution have been dispersed by mechanic homogenizer (WiseTis Homogenizer, HG-15D). Two different dispersion times (90 minute and 180 minute) and two different dispersion revolutions (7500 rpm and 15000 rpm) have been applied during preparation of GO dispersion. These GO dispersions products have been coagulated in the coagulation bath containing  $CaCl_2$ , ethanol and distilled water in order to obtain GO fiber. Besides, other coagulation bath containing NaOH, acetone and distilled water which were finalized either by vessel with acetone/distilled water mixture or by vessel with only acetone have been prepared (Figure 1). GO dispersed by 7500 rpm for 90 minute has been used for coagulation bath containing NaOH, acetone and distilled water. The continuous GO fiber in the range of 12 tex-16 tex have been produced by coagulation. The sample notation has been given in Table 1.

**Tests:** Mechanical and electrical properties of the GO fibers have been analyzed. Mechanical properties of the GO fibers were measured using a tensile tester (Usel, UNF15) according to the standard of ASTM D3822-07. The fiber has been tested at a crosshead speed of 1 mm/min and gauge length was adjusted to 10 mm. At least seven specimens were tested for each sample and average has been taken.

Table 1. Sample Notation

Sample Notation	Coagulation Bath	Rpm (Dispersion)	Time (Minute-dispersion)
GO- $CaCl_2$ -90-7500	$CaCl_2$	7500	90
GO- $CaCl_2$ -180-7500	$CaCl_2$	7500	180
GO- $CaCl_2$ -90-15000	$CaCl_2$	15000	90
GO-NaOH-20/80 DW/A	NaOH with 20/80 distilled water/Acetone last coagulation bath	7500	90
GO-NaOH-0/100 DW/A	NaOH with 0/100 distilled water/Acetone last coagulation bath	7500	90

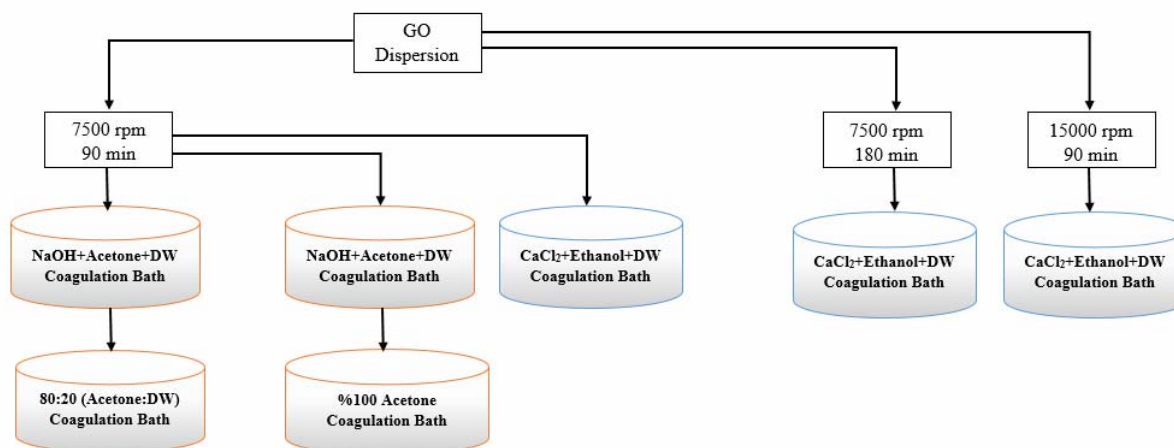


Figure 1. Schematic illustration of coagulation bath (DW: distilled water)

By using a two-probe system connected to Microtest 6370 LCR meter with four-wire system, the resistance measurements (R) were carried out. An electrical conductivity (K) was calculated in S/cm by the following formula.

$$K = L/R \times A \quad (1)$$

Where

K: coefficient of electrical conductivity

R: electrical resistance (ohm)

A: cross section area (cm<sup>2</sup>)

### 3. RESULTS AND DISCUSSION

GO fiber which has been obtained by coagulation in CaCl<sub>2</sub>, ethanol and distilled water has been shown in Figure 2. The mechanical properties of the samples have been given in Figure 3 and Figure 4. As seen from Figure 3 and Figure 4, there are clear differences on mechanical properties of samples. Highest breaking strength and breaking elongation belong to sample with coagulated by CaCl<sub>2</sub> and dispersed for 90 minute by 15 000 rpm. Dispersion rate has considerable positive effect on mechanical properties compared to dispersion time due to better dispersion of GO flake in the solution.

Coagulation bath containing NaOH and acetone results lower mechanical properties. This may be due to partially reduction of GO fiber which is a fast irreversible deoxygenation of graphene oxide and a stripping of functional groups from GO under basic (NaOH) conditions leading to an elimination of hydrogen bond between GO flakes (11). As known there are many type of reduction methods which decrease oxygen containing groups leading to an increase of C/O ratio. Some of the reduction methods (as in the case of reduction by Hydrazine or NaBH<sub>4</sub> which produce gas bubbles during reduction) result to an increase of rigidity (decrease of flexibility) of GO material (19, 20). It was observed that partially reduction of GO flakes due to NaOH results to harsher (rigid) GO structure. It may be possible that this harsher GO flakes could not be wrinkled easily during coagulation leading more porous and less contact (pinch) points between GO flakes which results to deterioration on mechanical properties. This lower mechanical property may also be due to the fast coagulation which is resulted from the low viscosity, high mobility and diffusion coefficient, high evaporation rate of acetone leading to highly porous and rigid structure in the GO fiber (11, 21). One of the reasons of having poor mechanical properties is the absence of CaCl<sub>2</sub>, since Ca<sup>2+</sup> divalent cations in coagulation bath with CaCl<sub>2</sub> react with carboxylate functional groups leading to an enhancement of mechanical properties of GO fiber due to ionic cross-linking (7, 8).

For the sample coagulated with NaOH-Acetone, as the content of acetone at the last bath increases, mechanical properties of GO fibers deteriorate. As the evaporation rate of solvents increases and surface tension of solvents (as in acetone) decreases, the bending and scrolling of GO flakes increases leading to more porous structure at the structure of GO fiber. Highly evaporative solvents and drying of these solvents also results crimped, wrinkled and rigid fiber and tightly pinch due to Van der Waals force (17). It is expected that this crimp, wrinkle and tightly pinch structure improves the mechanical properties, however highly porous and rigid

(harsh) structure in the GO fiber results a pronounced deterioration on mechanical properties.

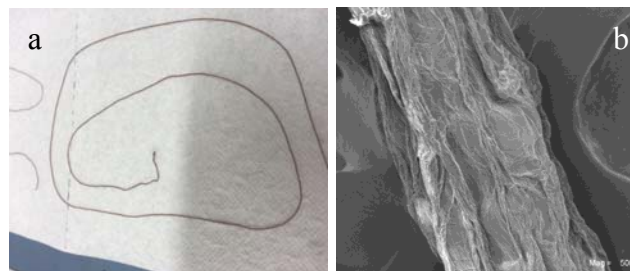


Figure 2. GO fiber coagulated with CaCl<sub>2</sub>, ethanol and distilled water, a- Fiber, b- SEM image of GO fiber

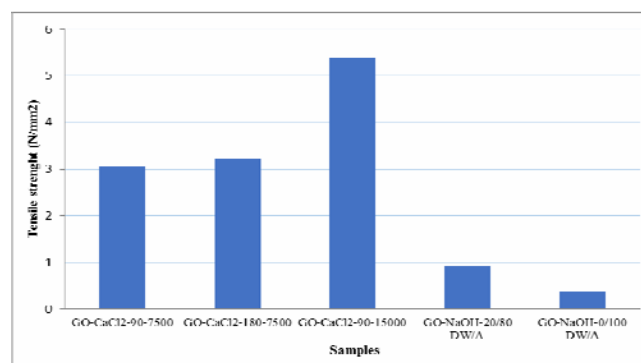


Figure 3. Tensile strenght of GO fiber samples

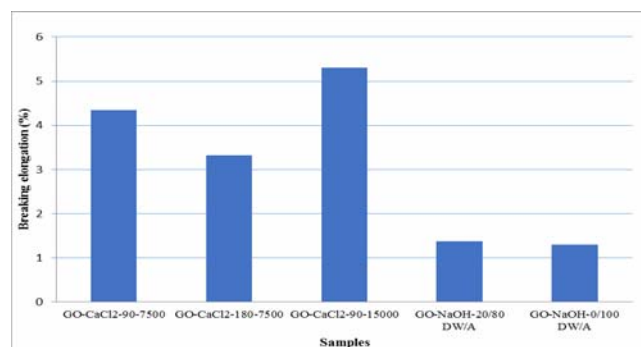


Figure 4. Breaking elongation of GO fiber samples

Electrical properties of the samples have been given in Table 2. As seen from Table 2, all of the samples have a similar electrical conductivity range (10<sup>-4</sup> S/cm) within the semi conductive material range. With regard to electrical conductivity, there are two opposite mechanism on the sample coagulated by NaOH-acetone, i.e., it is expected to an increase of electrical conductivity due to partially reduction, however it is also expected to a decrease of electrical conductivity due to porous structure (8, 11). Depending on process and material, sometimes partially reduction can be more evident and dominant than formation of porous structure leading to an increase of electrical conductivity of the materials. Conversely, if formation of porous structure is more evident than partially reduction, it is expected that the electrical conductivity of the material will decrease. Thus, the electrical conductivity of sample coagulated with NaOH-acetone depends on which mechanism has more dominant effect (22, 23).

#### 4. CONCLUSION

In this study, the dispersion time and dispersion revolution on mechanical and electrical properties of GO fiber have been analyzed. Further, one other study was also carried out in order to analyze the effect of last coagulation bath containing solvent with high evaporation rate on properties of GO fiber. This kind of material can be used for energy application, sensor, catalyst support, etc. From this study, following results have been concluded

- Dispersion rate has higher positive effect on mechanical properties than dispersion time.
- The samples lasted by %100 acetone has a lower mechanical properties than sample lasted by % 20/80 (distilled water/Acetone)

- There are clear differences on mechanical properties between samples. Among samples, highest mechanical properties belong to sample with coagulated by  $\text{CaCl}_2$  and dispersed for 90 minute by 15 000 rpm.
- Coagulation bath containing NaOH and acetone results lower mechanical properties than  $\text{CaCl}_2$  and ethanol.
- The change of dispersion time and dispersion revolution or last coagulation bath could not result any differences on electrical conductivity. With regard to electrical conductivity, all samples are in the semi conductive range ( $10^{-4}$  S/cm).

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**Table 2.** Electrical Conductivity of GO fibers (S/cm)

Sample	GO- $\text{CaCl}_2$ -90-7500	GO- $\text{CaCl}_2$ -180-7500	GO- $\text{CaCl}_2$ -90-15000	GO-NaOH-20/80 DW/A	GO-NaOH-0/100 DW/A
	2,5E-04	1,3E-04	1,9E-04	1,3E-04	1,04E-04

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