

Graphene Oxide Fiber with Different Exfoliation Time and Activated Carbon Particle

Nuray Uçar, Mervin Ölmez, Özge Alptöğ, Nilgün K. Yavuz, Ayşen Önen

Abstract—In recent years, research on continuous graphene oxide fibers has been intensified. Therefore, many factors of production stages are being studied. In this study, the effect of exfoliation time and presence of activated carbon particle (ACP) on graphene oxide fiber's properties has been analyzed. It has been seen that cross-sectional appearance of sample with ACP is harsh and porous because of ACP. The addition of ACP did not change the electrical conductivity. However, ACP results in an enormous decrease of mechanical properties. Longer exfoliation time results to higher crystallinity degree, C/O ratio and less d space between layers. The breaking strength and electrical conductivity of sample with less exfoliation time is some higher than sample with high exfoliation time.

Keywords—Activated carbon, coagulation by wet spinning, exfoliation, graphene oxide fiber.

I. INTRODUCTION

RESEARCHERS and industrialists have been fascinated by graphene due to its excellent properties, now a days it is being frequently studied for supercapacitors, solar cells, composite production, etc. Since graphene was produced directly in 2004 by Novoselov et al. [1] with very simple method. Graphene has been researched because of its excellent properties such as mechanical, thermal, chemical, electrical and economical properties resulting from low cost production, easy processing with high yield [2], [3]. Thus, it can have widespread usage in energy storage devices such as batteries, supercapacitors, fuel cells; sensing platforms, as a catalysis, biological applications, composite materials (with polymer, inorganic materials, organic crystals etc.), optical electronics, and so on [4]-[7].

Graphene (G) is the single carbon layer of graphite. It has the appearance of a 2-dimensional (2D) honeycomb structure and has sp^2 -bonded carbon atoms in its structure (Fig. 1) [8]. It can be directly obtained from graphite or may be obtained from reduction of graphene oxide.

Graphene oxide is obtained by the oxidation of graphite by different methods such as Brodie, Hummers or Staudenmaier. Among these, the most common method is Hummers [9]. The exfoliated GO sheets are highly oxidized and featured with the residual epoxides, hydroxides and carboxylic acid groups on their surfaces [6].

N. Uçar is with the Istanbul Technical University, Textile Engineering Department, Istanbul, Turkey (e-mail: ucarnuray@gmail.com).

M. Ölmez, Ö. Alptöğ, and A. Önen are with the Istanbul Technical University, Chemistry-Polymer Science and Technology Department, Istanbul, Turkey.

N.K. Yavuz is with the Istanbul Technical University, Energy Institute, Istanbul, Turkey.

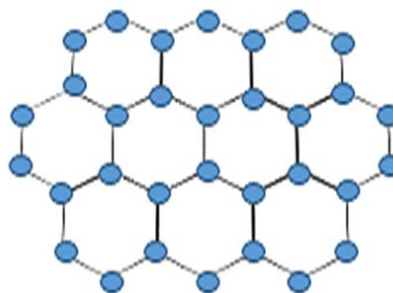


Fig. 1 Structure of graphene

With the discovery of the graphene, because of carbon fiber's outstanding performances, this unusual carbon-based material has also been explored for fiber production. As the properties of the GO fibers can be adjusted with various operations, it provides a wide working space for researchers [10]. Generally, graphene fibers are produced by spinning or hydrothermal method [10]. Among spinning methods [11], wet spinning method is very suitable for graphene oxide fiber production.

First studies on graphene fiber production starts from the 2011 years [8], [12].

General principle of continuous fiber production consists of three main steps:

- 1) Oxidation of graphite which is sometimes exfoliated by high temperature heating process,
- 2) The dispersion in suitable solvents such as water in order to disperse and separate the flakes from each other,
- 3) The coagulation of GO dispersion in suitable coagulation bath in order to obtain continuous GO fiber.

Until now, several studies focused on production of continuous graphene oxide fiber and reduction of graphene oxide fiber [8], [12]. Most of studies focused on the effect of coagulation bath, reduction type, graphite/graphene dimension and nozzle geometry [2]-[5], [13]-[16]. In addition to the conditions of fiber production, the structural properties of the graphene are also significant [4].

In some of studies, composite graphene or graphene oxide fiber production are also available by the presence of different additives and fillers such as Ag, SiO_2 , CNT, TiO_2 , Fe_2O_3 , MnO_2 , PANI, PAN [2], [7], [17]-[25]. According to work of Li et al., the way to increase the stiffness, toughness and conductivity is to remove the defects in the structure. They have pointed out that adding phenolic carbon into the dispersion increased mechanical properties. Phenolic carbon is produced from phenolic resin by annealing [7]. Xu and Gao have prepared polymer grafted graphene fiber (GF) by using

wet spinning method and they have observed high mechanical properties specially due to structural alignment [17]. Xu et al. have shown that Ag doped GFs can be produced continuously up to hundreds of meters long and they have predicted that these produced fibers can be applied in wearable electronics, micro cables etc. [18]. Zhao et al. have produced SiO₂ and fluorescent powder added fibers with a potential use in processes such as catalysts, sensing, and purification [19]. Huang et al. have developed GO hydrogel by mixing GO dispersion and NaDC (sodium deoxycholate) and then produced ribbon type fibers [20]. Dong et al. have reported Fe₃O₄ and TiO₂ doped GFs production. According to their report, these fibers show strong photocurrent response, so they can be applied in optoelectronic systems [21]. Furthermore, carbon nanotubes/graphene (CNT/G) hybrid fibers were studied by Cheng et al. and demonstrated high surface area and electrical conductivity [22]. Chen et al. have developed MnO₂ modified graphene sheets on GFs (MnO₂/G/GF) and it was used as a supercapacitor [23]. To obtain strong composite fiber, Liu et al. have fabricated PAN grafted GO fibers [24]. As a photovoltaic device, Yang et al. have produced wire-shaped device based on graphene/Pt composite fibers [25].

In this study, exfoliation of expandable Graphite Intercalation (GIC) in two different exfoliation process times (35 s and 45 s) and addition of activated nanoparticles (ACP) were performed. The effect of process parameters on samples has been analyzed by tensile tester and electrical conductivity tester, SEM, XPS, XRD.

II. MATERIALS AND METHODS

A. Materials

Expandable graphene-GIC with a thickness of 30 µm, diameter of 300 µm is supplied from Grafen Chemical Industries (Grafen Co). KMnO₄, H₂SO₄ and HCl are supplied from Merck, and NaNO₃ from Zag Ltd., ACP from Grafen Chemical Industries Co, (average particle dimension <100 nm, spherical, purity>95%). Distilled water and argon gas were used.

B. Production Methods

Exfoliation of expandable graphene was performed in a fixed-bed tube oven under the argon gas (0.5 standard liter per minute) at 1020 °C with two different process times, i.e., 35 second and 45 second. After exfoliation step, GO dispersion was prepared from exfoliated graphite flake by Hummers method [26]. Briefly, exfoliated graphite flakes, NaNO₃ and H₂SO₄ were mixed together and dispersed with a magnetic stirrer in an ice bath, followed by gradual addition of KMnO₄ to the mixture. Following several heating, cooling and dilution steps, the mixture was kept in distilled water (DW) for five days. Then, mixture with DW was treated with hydrogen peroxide (H₂O₂) for 24 hours to terminate the reaction. The color of the solution turned into yellow color. Then the solution washed in centrifuge (Nüve, NF800R) running at 5500 rpm, for three times with 1 M HCl solution. Afterwards, GO dispersion was washed several times by DW; the mixture

concentration was kept at 20 mg/ml. Later, GO solutions were dispersed by mechanical homogenizer (WiseTis Homogenizer, HG-15D) at 10000 rpm for 90 min. Some part of GO samples exfoliated at 1020 °C-35s has also been dispersed by 1 wt. % ACP. The dispersion was injected into the first, second and third coagulation bath respectively at a feed rate of 20 ml/h, through needle with 0.69 mm inner diameter. Coagulation steps of graphene oxide fiber are shown in Table I and Fig. 1.

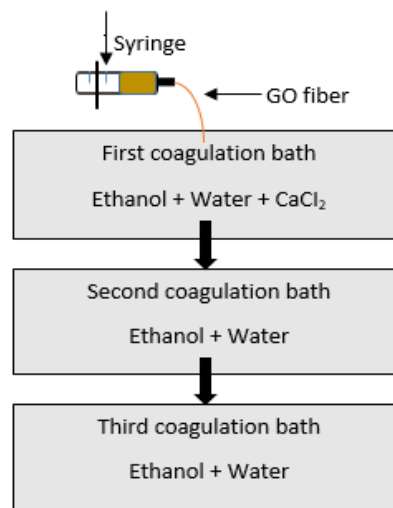


Fig. 1 Coagulation of GO fiber in three step

TABLE I
COAGULATION BATHS

Type	Substances
First coagulation bath	30 ml/70 ml (ethanol/water) + 5 % wt. CaCl ₂
Second coagulation bath	40 ml/60 ml (ethanol/water)
Third coagulation bath	50 ml/50 ml (ethanol/water)

C. Testing and Characterization

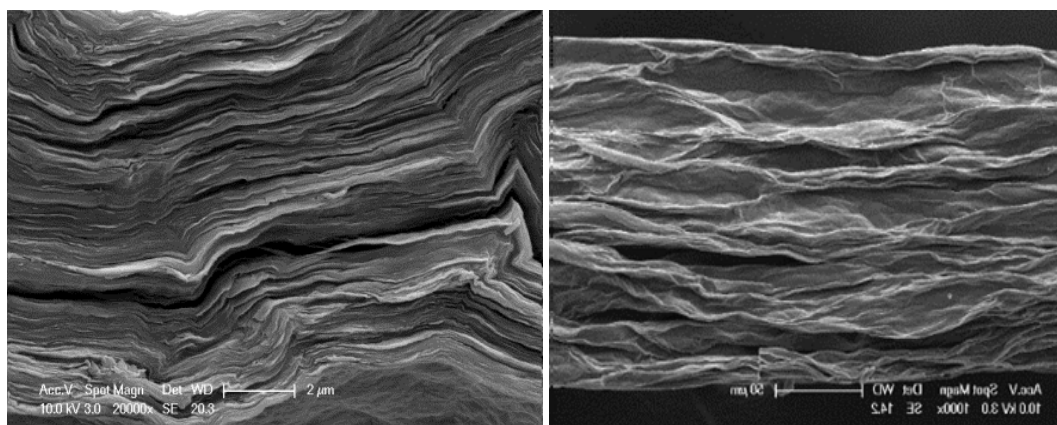
Tensile strength and elongation of the graphene oxide fiber samples were measured using a Usel, UNF 15 Tensile Tester at the gage length of 10 mm and a test speed of 1 mm/min according to the ASTM D3822-07 standard. Average value of 10 measurements has been taken. The electrical resistance values of the fiber samples in 1 cm length were measured with a two probe Microtest 6370 LCR meter. Average value of 10 measurements has been taken.

$$\rho = L/(A * R) \quad (1)$$

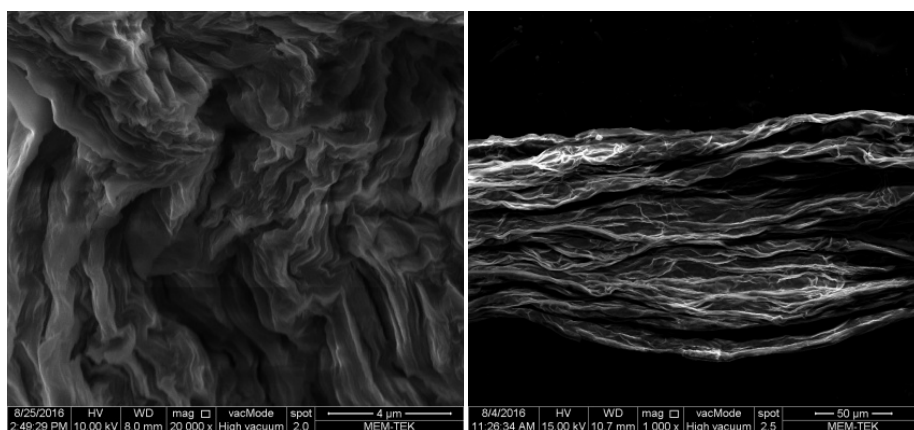
where; ρ = coefficient of electrical conductivity (S/cm), R = electrical resistance (ohm), A = cross sectional area of fiber (cm²) and L = Fiber length between the probes (cm).

The morphology of the GO fibers coated with Au/Pd (Quorum, SC7620) was characterized by Scanning Electron Microscopy (QUANTA FEG 200). The carbon and oxygen ratio has been calculated through the measurement results obtained from Thermo Scientific K-Alpha, X-ray Photoelectron Spectrometer. The XRD patterns of samples were taken from X-ray diffractometer (Bruker D8 Advance)

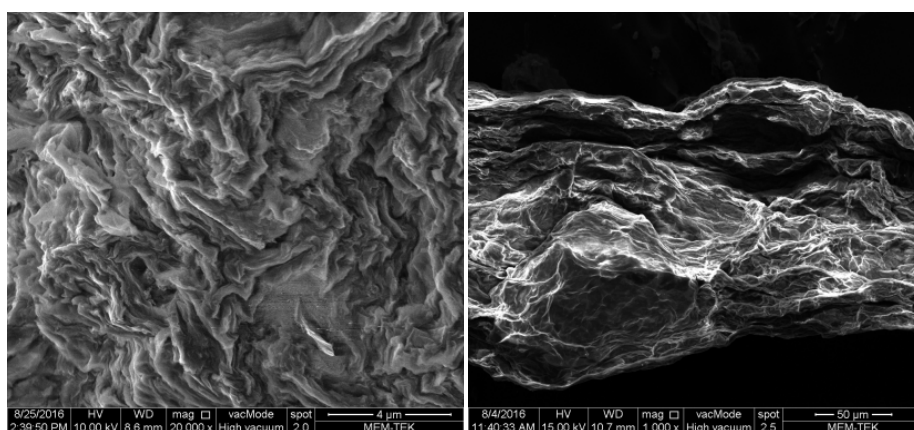
with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in order to analyse the crystalline structure.



(a)



(b)



(c)

Fig. 2 SEM of fibers, (a) 1020 °C-45 s, cross sectional and longitudinal appearance, respectively, (b) 1020 °C-35 s, cross sectional and longitudinal appearance, respectively, (c) 1020 °C-35 s fiber with 1 wt. % ACP (MH-Exf-1020C-35 s-ACP), cross sectional and longitudinal appearance, respectively.

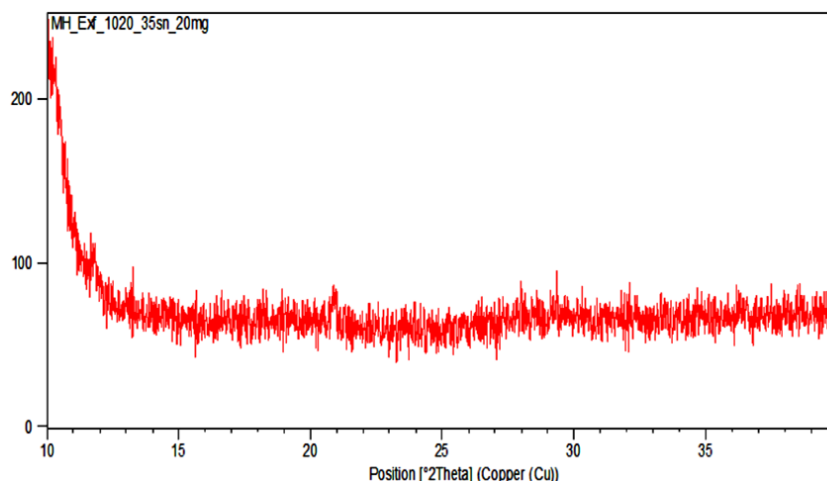


Fig. 3 XRD result of sample 1020°C-35s

III. RESULTS AND DISCUSSION

As seen from Fig. 2, appearance of sample with 1020 °C-45 s is smoother and more parallel structure than sample with 1020 °C-35 s and 1020 °C-35 s ACP. This may be due to fact that more exfoliation and separation of graphene flakes from each other or less and slowly coagulation during spinning. Harshly and porously cross sectional appearance has been observed for the sample with 1020°C-35 s ACP because of ACP.

As seen from Table II, sample with 1020 °C-45 s has less electrical conductivity than the other. The electrical conductivity did not be affected by the presence of ACP.

TABLE II
ELECTRICAL CONDUCTIVITY

Sample	Electrical conductivity (S/cm)	Coefficient of variation % CV
MH-Exf-1020C-35 s	$2,35 \cdot 10^{-3}$	21
MH-Exf-1020C-45s	$3,83 \cdot 10^{-4}$	22
MH-Exf-1020C-35 s-ACP	$1,05 \cdot 10^{-3}$	29

The mechanical properties of sample with 1020 °C-35 s (Table III) are better than sample with 1020 °C-45 s. This may be due to more functional group seen from less ratio of carbon to oxygen in XPS and also pinching of flakes to each other seen from SEM which provide strong bonding between layers. The excessive decrease in mechanical properties of sample with 1020 °C-35 s-ACP is because of ACP which causes harshly and porously structure seen from cross sectional appearance taken from SEM.

Higher crystallinity degree and lower d space between layer (2θ around 10 corresponding to graphene oxide as seen Fig. 3) has been observed at the sample with 1020°C-45s than sample 1020 °C-35s. This may be due to the longer heat treatment time under high degree which may lead to more reduction and higher degree of carbon as seen from higher C/O ratio (Table IV).

TABLE III
MECHANICAL PROPERTIES

Sample		Breaking extension (%)	Breaking strength (N/mm ²)
MH-Exf-1020C-35 s	Average	4,1	40,5
	% CV	26	27,1
MH-Exf-1020C-45s	Average	3,4	33,2
	% CV	29,4	27,4
MH-Exf-1020C-35 s-ACP	Average	5,7	3,9
	% CV	24,5	25,5

IV. CONCLUSION

ACP affects the morphology of fiber leading to harshly and porously structure. ACP leads to decrease of breaking strength, while it does not affect the electrical conductivity.

TABLE IV
THE RATIO OF CARBON AND OXYGEN AND CRYSTALLINITY PROPERTIES

Sample	The ratio of carbon and oxygen (C/O)	Crystallinity properties	
		Crystallinity %	d space (Å)
MH-Exf-1020C-35 s	2,32	73,2	5,8
MH-Exf-1020C-45s	3,38	88,2	3,3

The breaking strength and electrical conductivity of sample with 1020 °C-35s is some higher than sample with 1020 °C-45s which has a higher crystallinity degree and lower d space between layer.

ACKNOWLEDGMENT

This study is supported by TÜBİTAK (project number 114M524).

REFERENCES

- [1] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V. and Firsov A. A., "Electric field effect in atomically thin carbon film," *Science*, vol.306, 2004, 666.
- [2] Cong, H.P., Ren, X.C., Wang, P., Yu, S.H., "Wet-spinning assembly of continuous, neat, and macroscopic graphene fibers," *Scientific Reports*, vol.2, 2012, No.613, pp. 1-6.
- [3] Jalili R., Aboutalebi, S. H., Esrafilzadeh, D., Shepherd, R. L., Chen, J., Aminorroaya-Yamini S., Konstantinov, K., Minett, A. I., Razal, J. M.,

- Wallace, G. G., "Scalable one-step wet-spinning of graphene fibers and yarns from liquid crystalline dispersions of graphene oxide: Towards multifunctional textiles," *Advanced Functional Materials*, vol.23, 2013, pp.5345-5354.
- [4] Chen, L., He, Y., Chai, S., Qiang, H., Chen, F., Fu, Q., "Toward high performance graphene fibers," *Nanoscale*, vol.5, 2013, pp.5809-5815.
- [5] Shen H., Zhang L., Liu M., "Biomedical applications of graphene," *Theranostics*, March, vol.2 (3), 2012, pp. 283-294.
- [6] Huang X., Qui X., Boey F., Zhang H., "Graphene-based composites", *Chem. Soc. Rev.*, vol. 41, 2012, pp. 666-686.
- [7] Li M., Zhang X., Wang X., Ru Y., Qiao J., "Ultrastrong graphene-based fibers with increased elongation", *Nano Letters*, vol.16, 2016, pp. 6511-6515.
- [8] Xu Z., Gao C., "Graphene fiber: a new trend in carbon fibers," *Materials Today*, vol.18, 2015, pp. 480-492.
- [9] Paulchamy B., Arthi G., Lignesh B.D., "A Simple approach to stepwise synthesis of graphene oxide nanomaterial", *J Nanomed Nanotechnol*, vol. 6, 2015, No: 253. doi: 10.4172/2157-7439.1000253
- [10] Fan, T., Zhao C., Xiao Z., Guo F., Cai K., Lin H., Liu Y., Meng H., Min Y., and Epstein A. J., "Fabricating of high-performance functional graphene fibers for micro-capacitive energy storage". *Scientific Reports*, vol.6, 2016, pp. 1-8, doi: 10.1038/srep29534.
- [11] Hallett C. and Johnston A., *Fabric for Fashion: The Complete Guide:Natural and Man-made Fibers*, China: Laurence King Publishing Ltd, 2014, pp. 185-187.
- [12] Xu Z., Gao C., "Graphene chiral liquid crystals and macroscopic assembled fibres," *Nature Communications*, December, 571 (2), 2011, pp. 1-9.
- [13] Pei, S., Cheng, H., "The reduction of graphene oxide," *Carbon*, vol.50, 2011, pp.3210-3228.
- [14] Stankovich, S., Dikin, D.M., Piner, R.D., Kohlaas, K.A., Kleinhammes A., Jia, Y., Wu, Y., Nguyen, S.T., Ruoff, R.S., "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *Carbon*, vol.45, 2007, pp.1558-1565.
- [15] Aboutalebi S.H., Jalili, R., Esrafilzadeh, D., Salari M., Gholamvand Z., Yamini S.A., Konstantinov, K., Shepherd, R.L., Chen, J., Moulton, S.E., Innis, P.C., Minett, A.I., Razal, J.M., Wallece, G.G., "High-performance multifunctional graphene yarns: toward wearable all-carbon energy storage textiles," *AcsNano*, vol.8, 2014, No.3, pp. 2456-2466.
- [16] Xiang, C., Young C., Wang X., "Large flake graphene oxide fibers with unconventional 100% knot efficiency and highly aligned small flake graphene oxide fibers," *Advanced Materials*, September, vol.33 (25), 2013, pp. 4592-4597.
- [17] Xu Z., Sun H., Zhao X., Gao C., "Graphene in macroscopic order: Liquid crystals and wet-spun fibers," *Advanced Materials*, vol.25, 2013, pp.188-193.
- [18] Xu Z., Liu Z., Sun H., "Highly electrically conductive ag-doped graphene fibers as stretchable conductors," *Advanced Materials*, June, vol.23 (25), 2013, pp. 3249-3253.
- [19] Zhao Y., Jiang C., Hu C., "Large-scale spinning assembly of neat, morphology-defined, graphene-based hollow fibers," *Acs Nano*, February, vol.3 (7), 2013, pp. 2406-2412.
- [20] Huang G., Hou C., Shao Y., Wang H., Zhang Q., Li Y. and Zhu M., "Highly strong and elastic graphene fibers prepared from universal graphene oxide precursors," *Scientific Reports*, 4, 2014, 4248.
- [21] Dong Z., Jiang C., Cheng H., Zhao Y., Shi G., Jiang L., Qu L., "Facile fabrication of light, flexible and multifunctional graphene fibers," *Advanced Materials*, vol.24, 2012, pp. 1856-1861.
- [22] Cheng H., Dong Z., Hu C., Zhao Y., Hu Y., Qu L., Chen N. and Dai L., "Textile electrodes woven by carbon nanotube-graphene hybrid fibers for flexible electrochemical capacitors," *Nanoscale*, vol.5, 2013, 3428.
- [23] Chen Q., Meng Y., Hu C., Zhao Y., Shao H. Chen N., Qu L., "MnO₂-modified hierarchical graphene fiber electrochemical supercapacitor," *Journal of Power Sources*, vol.247, 2014, pp.32-39.
- [24] Liu Z., Xu Z., Hu X., and Gao C., "Lyotropic liquid crystal of polyacrylonitrile-grafted graphene oxide and its assembled continuous strong nacre-mimetic fibers," *Macromolecules*, 46, 2013, 6931.
- [25] Yang Z., Sun H., Chen T., Qiu L., Luo Y., Peng H., "Photovoltaic wire derived from a graphene composite fiber achieving an 8.45% energy conversion efficiency," *Angewandte Chemie*, vol.125 (29), 2013, 7693.
- [26] Ucar N, Gokceli G., Yuksek I. O, Onen A, Yavuz N. K., "Graphene oxide and graphene fiber produced by different nozzle size, feed rate and reduction time with Vitamin C," accepted for publication in *Journal of Industrial Textiles*.