Journal of Materials and Electronic Devices 4 (2022) 22-26

Preparation and Characterization of Functional Graphene Based Dispersions for Wearable Electronics

Onur DEMİREL[1,2], Fulden KAYGINOK[1], Alp Eren GÜROL[1], Sibel KASAP*[1]

[1]ASELSAN Advanced Materials Technologies Research Division, 34906, Teknopark Istanbul, Istanbul, Turkey
[2]Sabancı University, Faculty of Engineering and Natural Sciences, 34956, Orta Mahalle, Tuzla, İstanbul, Turkey

With the development of technology, the interest in wearable electronics has increased and graphene/its derivatives with superior electrical properties have also found a place in this field. However, during the integration of graphene into the different systems, encountering interlayer stack and agglomeration problems has led to search for new solutions.

In this study, we tried to both overcome the existing problems in graphene-based systems and obtain electrically conductive graphene dispersion. The graphene dispersion was produced by using polyvinylpyrrolidone as a stabilizer to obtain a stable dispersion and functionalized by adding silver nanoparticles to increase the electrical conductivity of dip coated samples. Structural characterizations were performed by Raman and Scanning Electron Microscopy analysis while Transmission Line Measurement was used to examine electrical properties of the samples and rheological analysis was conducted to investigate structural change with the addition of silver nanoparticles.

Keywords: *graphene, conductive dispersions, wearable electronics, graphene characterization, dispersion characterization*

Submission Date: 01 November 2022
Acceptance Date: 02 December 2022

**Corresponding author: skasap@aselsan.com.tr*

1. Introduction

As wearable technologies advance and their market grow rapidly, the need for inexpensive and easy to manufacture electronic devices arises. Wearable technologies require flexible, bendable, chemically stable electrically conductive materials with low cost production and application methods. Evidently, flexible electronics play a major role for new wearable devices. Compared to traditionally used vapour deposition techniques, printing techniques such as screen printing, inkjet printing, gravure printing are cost effective and easy to use in mass production, avoids heavy expenses like usage of vacuum chamber. Moreover, multiple components could be printed at the same time. While, formulating conductive dispersions could be applied at printing methods, printing remains as a major challenge [1,2].

To date, the most conductive systems include dispersed metal nanoparticles such as gold, silver and copper as main material. Dispersions containing only metal nanoparticles are either too expensive, tend to oxidize or require high heat for annealing treatments which limits the substrate choices and production methods [2]. Although, conductive polymers are studied, their conductivity or price are not competitive with metal nanoparticle-based dispersions [3]. Therefore, there is a need for development of new materials for conductive dispersions.

Graphene is a two-dimensional material formed by single layer sp-2-hybridized carbon atoms. Graphene distinguishes from other semi-conductor materials by having linear energy spectrum near Fermi level instead of parabolic. The unique electronic structure allows charge carriers to move as massless Dirac fermions [4]. The distinctive features makes graphene an alternative for metals for wide spread of applications. Furthermore, graphene exhibits cheaper and better producibility than other carbon-based materials. Besides its advantages, due to hydrophobic nature of graphene, it is hard to disperse in water and hard to form interconnected network when the dispersion is dried. Adding dopant elements, stabilizers, surfactants and using optimized dispersing methods could overcome these obstacles. The chosen dopant should not need high annealing temperatures or affect the viscosity and surface tension [5,6].

Combining the advantages of graphene and metal nanoparticles have potential to achieve inexpensive, and efficient conductive dispersions. However, it was stated that the system must have good dispersion in order to proceed efficiently [7]. One of the most frequently used methods to prevent agglomeration and to separate layers of materials having strong van der Walls forces between layers, such as graphene nanoplatelets (GNPs), is liquid exfoliation technique. Also, its process parameters must be well-defined for successful and efficient production [8]. Within these parameters, the choice of solvent has a critical role. In the literature, solvents exhibiting low boiling point such as water, propanol, butanol have been used, as well as the ones with high boiling points such as dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) [9-13]. Since these chemicals having high boiling point show high surface tension, they exfoliate graphene layers more easily and effectively than others [14]. However, high surface tension cannot play an active role in breaking the force between the hydrophobic GNP layers. To overcome this problem, various stabilizers are added to the liquid system to facilitate dispersion and prevent agglomeration. It was stated that dispersions remained stable and the number of aggregates was greatly reduced by the use of non-toxic polyvinyl pyrrolidone (PVP) used as a stabilizer [15,16].

In this study, graphene dispersion (Gr) and Ag NPs decorated graphene hybrid dispersion (Ag NPs/Gr) were produced using PVP stabilizer. The dispersions applied on cellulose paper using simple dip-coating method and morphology. Then, the structural change and electrical resistivity of the dispersions were investigated.

2. Experimental

2.1. Materials:

All chemicals used were of analytical grade and they were purchased from Sigma-Aldrich. The details of the chemicals are as follows: GNPs with average particle size 25 μm. PVP with an average molecular weight of 1 300 000. Ethylene glycol (EG) with 99.9% purity and silver nanoparticles (Ag NPs) in EG with average diameter 180 nm.

2.2. Preparation of Graphene Dispersion

Gr dispersion was prepared by a modified polyol method. Firstly, 0.5 g PVP was added into 50 mL of EG solution and the mixture was stirred at ambient temperature for 1 hour (h) to obtain bright solution. After that, 2.5 g of GNPs was poured into the solution. The viscous slurry was then placed in the sonicator (Bandelin Sonoplus probe sonicator, TS-109 Probe) with a water bath at 70% power for 1 h.

2.3. Preparation of Ag NPs/Gr Hybrid Dispersion:

Ag NPs/Gr hybrid dispersion was prepared by mixing the viscous GNPs slurry with different amount of colloidal suspension of Ag NPs (1, 5, and 10 wt.%) in EG. The mixture then was sonicated as defined conditions above.

2.4. Preparation of coated paper films:

Dispersion coated cellulose paper films were fabricated by dip-coating method, followed by thermal annealing. For the dip coating process, cellulose papers were cut on 1 cm x 1 cm and then they were immersed in the prepared dispersions at the same soaking time (30 second). Finally, the coated papers were dried in an oven at 80℃ for 1 h.

2.5. Characterization:

Scanning electron microscopy (SEM, Zeiss Gemini 1530) and Raman spectroscopy (Renishaw inVia Reflex, at 532 nm) were used to structurally characterize the samples. The sheet resistance (R_s) of the graphene samples was measured by the Transmission Line Measurement (TLM) technique. Rheological measurements (Anton Paar) were conducted to analyse microstructural change with the addition of nanoparticles. Firstly, strain sweep test was performed to determine linear viscoelastic region at 25℃. Then, frequency sweep test was applied in the range between 0.1-100 rad/s.

3. Results

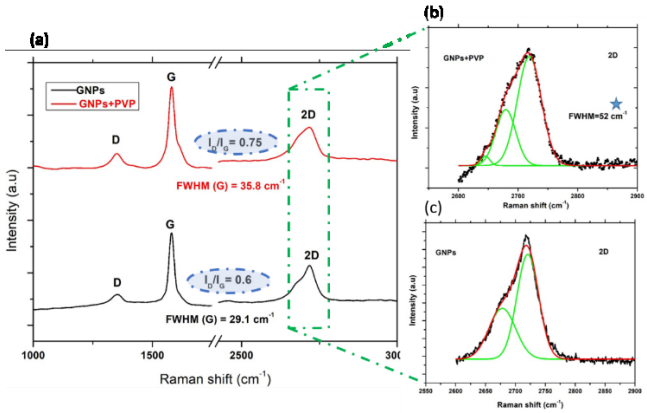

Fig.1. (a) Raman spectrum of GNPs and GNPs+PVP, (b) 2D band of GNPs+PVP, (c) 2D band of GNPs.

Raman spectroscopy which is a non-destructive method, is used for identifying and characterizing different types of carbon-based materials. Figure 1 shows Raman spectra at 532 nm for GNPs powder and dispersion of graphene in PVP. In both of the spectra, 2D, G and D peaks are located at ~ 2700 cm^{-1}, 1576 cm^{-1} and 1359 cm^{-1} as expected for graphene [17].

To identify the number of graphene, analysis of 2D peak shape is a one of the most common methods. In this study, the deconvolution technique was applied to explain the changes between the Raman spectra of GNPs and GNPs+PVP. The deconvolution of 2D band in Raman spectra of GNPs revealed that GNPs was graphitic form. On the other hand, for GNPs+PVP, the 2D band split into several overlapping modes suggesting that the dispersions consist of few-layer graphene. In addition, the average full width half maximum (FWHM9 for the 2D band was found to be 52 cm^{-1}, which is the range for few layer graphene sheets.

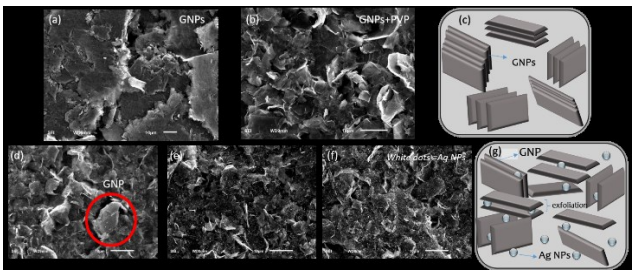

Fig.2. SEM images for (a) GNPs flakes, (b) Gr Dispersion by using PVP on mica, (c) illustration of Gr dispersion, Ag NPs-Gr hybrid coated cellulose papers; (d) 1 wt.%, (e) 5 wt.%, (f) 10 wt.%, and (g) illustration of Ag NPs/Gr hybrid dispersions.

In Figure 2, the SEM images of the pure GNPs flakes, Gr dispersion coated paper and Ag NPs-Gr hybrid dispersion coated papers are illustrated. The surface of Gr dispersion on mica which is quite smoother than pure GNPs flakes shown in Figure 2 a and b. The decrease in the topological defects of the GNPs flakes is due to addition of PVP. In figure d, e, and f, white dots represent Ag NPs. As the amount of Ag NPs increases, more Ag NPs are intercalated into the GNPs sheets.

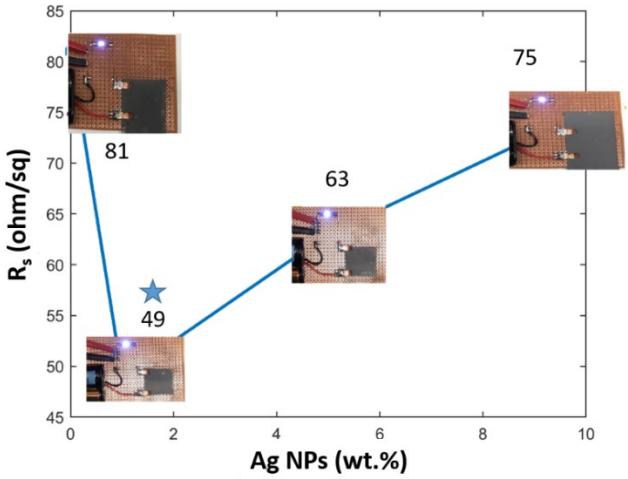

Fig.3. Sheet resistance of the dispersion coated samples as a function of Ag NPs.

TLM was used to investigate the changes in the sheet resistance (R_s) with respect to the Ag NPs concentration. The correlation is visible in Figure 3. The Rs value of 49 ohm/sq dramatically decreases when there is 1 wt.% of Ag NPs in the Gr dispersion. On the other hand, it was observed that the R_s value shows an increasing trend when the Ag NPs concentration increases. The R_s value for 5 wt.% and 10 wt.% samples was calculated to be 63 and 75 ohm/sq, respectively. This tendency might be attributed to a possible agglomeration of Ag NPs. As the concentration increases, Ag NPs tend to agglomerate and diffuse into graphene flakes, causing defects.

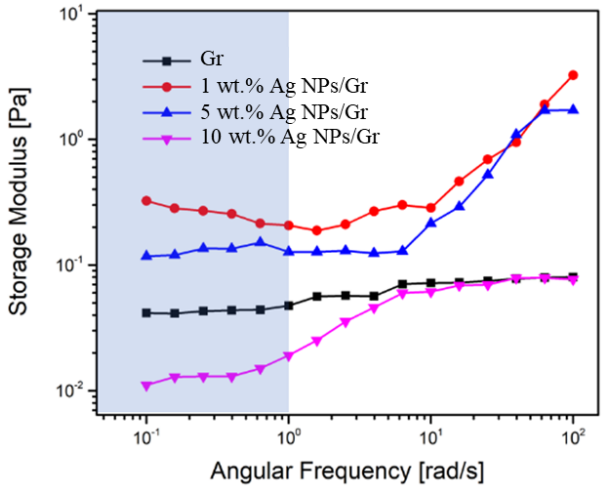

Fig.4. Storage modulus versus angular frequency plots of the dispersions.

Analysis of rheological behavior is one of the strongest tools to examine the microstructural change in the suspensions. Focusing on the low frequency region (up to 1 rad/s), the storage modulus increases with the addition of 1 and 5 wt.% Ag NPs, which indicating solid network formation between Ag NPs and Gr. However, higher amount of Ag NPs may destroy the network between GNPs, causing decrease in the storage modulus. Results were consistent with electrical resistivity values, which means electrical conductivity related with network formation.

4. Conclusion

In this study, highly conductive Ag NPs/Gr Hybrid dispersion was developed. The obtained hybrid dispersion was applied on cellulose based papers by using dip-coating method and structural and electrical characterizations were performed. The electrical tests showed that the increasing amount of silver nanoparticle concentration causes a negative effect on the Rs value. The Rs value was found to be 49 ohm/sq at 1 wt.% Ag NPs concentration. It can be concluded that the hybrid dispersions are promising candidates for wearable electronics applications.

References

[1] E. B. Secor, P. L. Prabhumirashi, K. Puntambekar, M. L. Geier, M. C. Hersam, Inkjet printing of high conductivity, flexible graphene patterns. The journal of physical chemistry letters, 4(8) (2013) 1347-1351.

[2] W.Yang, C.Wang, Graphene and the related conductive inks for flexible electronics. Journal of materials chemistry C, 4(30) (2016) 7193-7207.

[3] E.Jabari, F.Ahmed, F. Liravi, , E. B.Secor, L.Lin, E. Toyserkani, 2D printing of graphene: a review. 2D Materials, 6(4) (2019) 042004.

[4] S. K.Tiwari, S.Sahoo, N.Wang, A.Huczko, Graphene research and their outputs: Status and prospect. Journal of Science: Advanced Materials and Devices, 5(1) (2020) 10-29.

[5] Y. I. Lee, S.Kim, S. B. Jung, , N. V.Myung, Y. H. Choa, Enhanced electrical and mechanical properties of silver nanoplatelet-based conductive features direct printed on a flexible substrate. ACS applied materials & interfaces, 5(13) (2013) 5908-5913.

[6] L. Y. Xu, G. Y.Yang, H. Y. Jing, J.Wei, Y. D. Han, Ag–graphene hybrid conductive ink for writing electronics. Nanotechnology, 25(5) (2014) 055201.

[7] Y. Xu, I. Hennig, D. Freyberg, A. J.Strudwick, M. G. Schwab, T.Weitz, K. C. P. Cha, Inkjet-printed energy storage device using graphene/polyaniline inks. Journal of Power Sources, (2014) 248, 483-488. [8] A.MOOSA, M. ABED, Graphene preparation and graphite exfoliation. Turkish journal of Chemistry, 45(3), (2021)493-519.

[9] A. O'Neill, U. Khan, P.N. Nirmalraj, J. Boland, J.N. Coleman Graphene Dispersion and Exfoliation in Low Boiling Point Solvents. J. Phys. Chem. C. (2011) 115:5422–5428.

[10] Buzaglo M., Shtein M., Kober S., Lovrincic R., Vilan A., Regev O. Critical parameters in exfoliating graphite into graphene. Phys. Chem. Chem. Phys. (2013) 15:4428–4435.

[11] Tanna V.A. W., B.M.Yavitt, C. Dimitrakopoulos, H.H. Winter Fast Production of High-Quality Graphene via Sequential Liquid Exfoliation. ACS Appl. Mater. Interfaces, 7 (2015) 27027–27030.

[12] U.Khan, A.O'Neill, M.Lotya, S. De, J.N. Coleman, High-Concentration Solvent Exfoliation of Graphene. Small, 6 (2010) 864–871.

[13] P. Blake, P.D. Brimicombe, R.R.Nair, T.J.Booth, D. Jiang, F.Schedin, L.A.Ponomarenko, S.V. Morozov, H.F. Gleeson, E.W.Hill, Graphene-based liquid crystal device. Nano Lett., 8 (2015)1704–1708.

[14] Y.Hernandez, V.Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T. McGovern, B.Holland, M.Byrne, Y.K Gun'Ko.,High-yield production of graphene by liquid-phase exfoliation of graphite. Nat. Nanotechnol.,3 (2008), 3:563–568.

[15] A. S.Wajid, S. Das, F.Irin, H. T. Ahmed, J. L. Shelburne, D.Parviz, M. J. Green, Polymer-stabilized graphene dispersions at high concentrations in organic solvents for composite production. Carbon, 50(2) (2012), 526-534.

[16] A. B. Bourlinos, V.Georgakilas, R. Zboril, T. A. Steriotis, A. K.Stubos, C. Trapalis, Aqueous-phase exfoliation of graphite in the presence of polyvinylpyrrolidone for the production of water-soluble

graphenes. Solid State Communications, 149(47-48) (2009) 2172-2176.

[17] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim. Raman Spectrum of Graphene and Graphene Layers, Phys. Rev. Lett. 97 (2006) 187401.