

PROCESSING AND CHARACTERIZATION OF NOVEL GRAPHENE CONTAINING INKS

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ABSTRACT

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Scientific and industrial community currently has an increased interest in printed electronics due to its many advantages. Metallic nanoparticles and conductive polymers are mostly used in the processing of commercial conductive inks. There is extensive research and development efforts on alternative materials as conductive fillers due to high cost, chemical instability in air and liquid media of widely used fillers. Graphene materials comprised of a single layer or multiple layers of graphene flakes have recently attracted great interest and used in applications as an excellent conductive filler due to its optical transparency, high conductivity, and flexibility.

The aim of this MSc work was to prepare graphite and carbon black based conductive inks. Effects of graphite (G) to carbon black (CB) ratio and the use of exfoliation liquid on conductivity, rheology and particle size distribution were investigated for graphite containing conductive inks. Inks with the lowest resistance of 0.02 k Ω was obtained by using ball milling in N-metil-2-pirrolidon (NMP) as exfoliation liquid with the lowest particle size with an average of 18.0 μm . Inks prepared in this work showed shear thinning behavior independent of the exfoliation liquid used in their preparation. The highest thixotropy was measured in water exfoliated ink with 1801 Pa.s⁻¹ and this dispersion had the lowest conductivity.

A series of inks with different graphite to carbon black ratios were prepared under similar conditions. The lowest resistance 0.045 k Ω was determined at a graphite to carbon black ratio of 1 by using ethylene glycol as an exfoliation liquid. The use of ethylene glycol in commercial ink preparation may be advantageous due to its lower cost and environmentally friendly chemical properties. The highest degree of thixotropy and viscosity was measured in ink prepared at G/CB ratio of 0.5. This ink also had the highest resistance due to low amount of graphite compared to carbon black which indicated the critical importance of G/CB ratio.

ÖZET

ÖZGÜN GRAFEN İÇEREN MÜREKKEPLERİN HAZIRLANMASI VE KARAKTERİZASYONU

Günümüzde birçok avantajı nedeniyle basılı elektroniklere olan ilgi bilimsel ve endüstriyel topluluk tarafından artmıştır. Ticari iletken mürekkeplerin işlenmesinde çoğunlukla metalik nanopartiküller ve iletken polimerler kullanılır. Yaygın olarak kullanılan bu dolgu maddelerinin yüksek maliyeti, hava ve sıvı ortamdaki kimyasal kararsızlığı nedeniyle başka alternatif malzemeler üzerinde kapsamlı araştırma ve geliştirme çalışmaları yapılmaktadır. Tek bir katmandan veya çok sayıda grafen pul katmanından oluşan grafit malzemeleri, son zamanlarda optik şeffaflığı, yüksek iletkenliği ve esnekliği nedeniyle uygulamalarda mükemmel bir iletken dolgu maddesi olarak kullanıldığı için büyük ilgi görüyor.

Bu yüksek lisans çalışmasının amacı, grafit ve karbon siyahı bazlı iletken mürekkepler hazırlamaktır. Grafitin karbon karası oranına ve eksfoliasyon sıvısının iletkenlik, reoloji ve parçacık boyutu dağılımı üzerindeki etkileri, grafit içeren iletken mürekkep için araştırılmıştır. Eksfoliasyon sıvısı olarak N-metil-2-pirrolidon (NMP) içinde bilyeli öğütme kullanılarak en düşük partikül boyutuna ve ortalama 18.0 μm ile 0.02 $\text{k}\Omega$ ile en düşük dirence sahip mürekkepler elde edilmiştir. Bu çalışmada hazırlanan mürekkepler kesme gerilimi altında inceme davranışı göstermektedir ve bu özellik kullanılan eksfoliasyon sıvısından bağımsızdır. En yüksek tiksotropi, 1801 $\text{Pa}\cdot\text{s}^{-1}$ ile suyla eksfoliasyon edilmiş mürekkepte ölçülmüştür ve bu dispersiyon en düşük iletkenliğe sahiptir.

Benzer koşullar altında farklı grafit-karbon siyahı oranlarına sahip bir dizi mürekkep hazırlanmıştır. En düşük direnç 0.045 $\text{k}\Omega$, eksfoliasyon sıvısı olarak etilen glikol kullanılarak grafitin karbon siyahına oranını 1 olduğunda ölçülmüştür. Etilen glikolün ticari mürekkep hazırlamada kullanılması, düşük maliyeti ve çevre dostu kimyasal özellikleri nedeniyle kullanılması avantajlı olabilir. En yüksek tiksotropi ve viskozite derecesi, 0.5 G/CB oranında hazırlanan mürekkepte ölçülmüştür. Bu mürekkep ayrıca G/CB oranının kritik önemini gösteren karbon siyahına kıyasla düşük grafit miktarı nedeniyle en yüksek dirence sahiptir.

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LIST OF SYMBOLS/ABBREVIATIONS

Greek Letters

$\dot{\gamma}$	Shear rate
τ	shear stress
η	viscosity
Ω	ohm

CHAPTER 1

INTRODUCTION

Materials are well known to be the main driving force for the growth of technology and human civilization. Traditional electronic devices which are produced with metal etching uses some significant raw materials. Developments in material science and technology caused dramatic improvements and novelties of new electronic product properties like flexibility and miniaturization. Printed flexible electronic devices produced through the application of conductive inks on various substrates can create innovative electronic devices.

Conductive inks are the main component which will affect the future of printable electronics. Generally conductive inks have three main components which are conductive material, solvent, and resin. Conductive materials are mainly responsible for the electrical conductivity of conductive inks. Various studies regarding conductive materials in inks have been conducted. Metal-based nanoparticle containing inks attracted a major interest due to their electrical conductivity among these various ink formulations. These metal-based inks however have many problems like high cost, high sintering processes after application and even oxidation problems for some of these inks.

The interest to the use of graphene in conductive ink formulations increased in recent years due to the outstanding electrical and mechanical properties of graphene. Despite its excellent properties, wide-spread use of graphene at an industrial level is limited due to the problems in the large-scale production. Intensive research efforts therefore currently are concentrated on the improvement of production and application methods of graphene-based materials (Stafford et al., 2018).

There are many recent R&D articles on the use of graphene in conductive inks for printed electronics. Graphene has single atomic layer of carbons in 2D honeycomb lattice. This structure ensures sp^2 bonded carbon atoms. Graphene is accepted as the thinnest, most flexible, and strongest material that conducts both electricity and heat (Jaworski et al., 2013).

Graphene production methods can be divided into two main categories which are bottom-up and top-down methods. Bottom-up methods such as chemical vapor deposition (CVD), epitaxial growth depend on production of graphene on the various substrates. On

the other hand, top-down methods such as liquid phase exfoliation (LPE) and mechanical exfoliation depend on graphene production from bulk carbon sources. LPE is a straightforward and a high-yield method among these methods which was also the reasoning behind its use in this thesis.

Liquid phase dispersion of graphene could be divided into two main parts which are the graphene exfoliation and the preparation of a stable dispersion of graphene. The main aim of graphene exfoliation is to overcome Van-der Waals forces holding the graphene layers in structure and the separation of the graphene layers. Selection of solvent-resin type and conductive material ratios are important for liquid medium stability of graphene.

Different printing techniques such as screen printing, 3D printing, inkjet printing could be used for application of graphene based conductive inks to various surfaces. That's why rheological properties and particle size distribution of conductive inks must be optimized. This thesis was focused on the investigation of the effects of the exfoliation liquid and graphite/carbon black ratio on particle size distribution and rheological properties of the inks and finally on the resistances of the printed surfaces.

CHAPTER 2

CONDUCTIVE INKS

Importance of conductive inks are increasing due to the accelerating use in manufacturing/application areas in printed electronics like circuits, diodes, supercapacitors, and batteries. Conductive inks have a wide range of application areas such as organic light-emitting diodes, organic and inorganic photovoltaics, radio-frequency identification, transistors, solar cells. The probability of lighter, thinner, and more flexible electronics prepared with printing increase importance of printed electronics for future. Traditionally, electronic devices are manufactured by Silicon (Si) technology whose surfaces are further processed by photolithography, vacuum deposition, and electroless plating processes. All these production methods require high costs and many chemicals. Traditionally produced electronic devices produce chemical wastes which affect environment in a bad manner. Disposal of such wastes also increase costs of the electronic devices. Compared to these traditional methods, printing conductive inks provide rapid, cost effective and eco-friendly way for printed electronics on many substrates. Flexible electronics will solve many challenges of electronic devices in coming decades (Leng et al., 2019).

Conductive inks must be inexpensive, easily producible and offer good adhesion properties with high electrical conductivity. Conductive inks have become a topic of interest and becomes an important participant in printing industry. Figure 1. shows dramatic increase of published number papers on conductive inks between 2009 and 2018 (Saidina et al., 2019).

Conductive inks mainly contain four different components which are conductive component, resin, solvent, and additive. Resins are used for the dispersion and adhesion of conductive particles. Solvents are used for the adjustment of rheological and printing properties of inks. Additives are generally used for effective processibility and dispersion of conductive inks. Particle dispersions are most often used group of methods for preparation of conductive inks. Several inks with particles of Ag, Cu, Ni, Al, P, Si, C can be produced.

Printability of conductive inks depend on the nature of the components, their extents in the dispersion, particle size distribution and type of the conductive component and the properties of application surface. Conductivity of the dried printed inks depend on materials use in an optimum level in the ink formulation during their preparation process. Industrial printing methods such as inkjet printing, screen printing, flexography and gravure could be used for manufacturing of printed electronics.

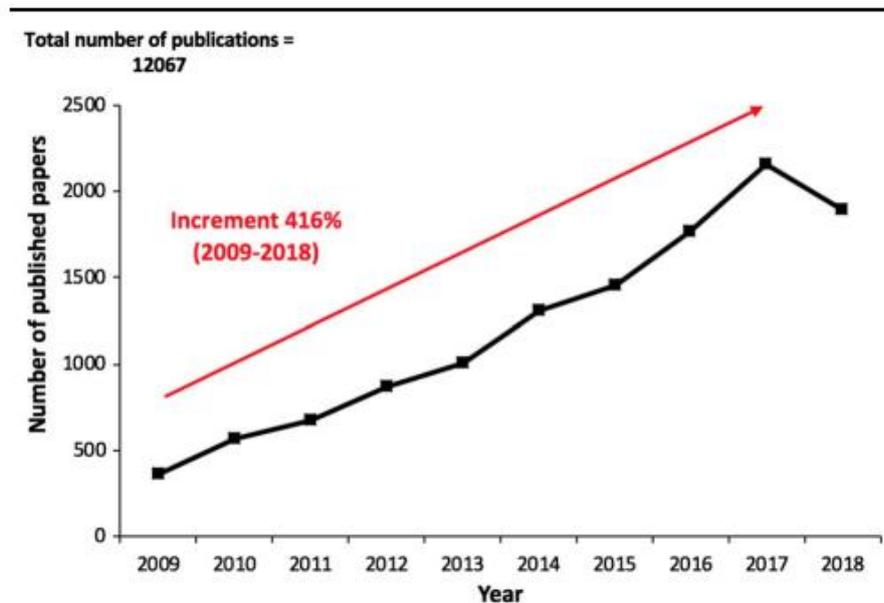


Figure 1. Published conductive ink papers between 2009-2018. Data was taken from Web of Science and Scopus. (Source: Saidina et. al, 2019)

Metal particle containing inks such as gold nanoparticles (AuNPs), silver nanoparticles (AgNPs) and copper nanoparticles (CuNPs) dominate the conductive ink market due to their higher conductivity. Metal particles of gold and silver containing inks are expensive and these inks often have stability problems. For instance, high cost and electromigration properties of silver restricts its industrial application. Another drawback of these inks is the relatively high sintering temperatures necessary to ensure conductivity which limits application of these inks with flexible substrates. Copper is the biggest alternative to silver and gold due to its high bulk conductivity but copper containing inks have oxidation problems which affects their electrical conductivity and increase sintering temperatures.

There is a great effort to solve problems of metal particle containing inks. These efforts are mainly concentrated on development of carbon-based conductive inks due to their excellent electrical properties. Studies related with carbon based conductive inks

specifically proceed with graphene-based inks. Graphene inks have many advantages over the metal particle containing conductive inks like offering sintering free application on various substrates. Despite the huge potential of graphene inks the use of these inks is currently very limited due to the absence of large volume production techniques and frequent usage of some toxic solvents making these inks comparatively expensive. For instance, commercial graphene based conductive ink price is higher than \$500 per 10 ml. The improvement of graphene production and printing technologies involving graphene inks however will lower the application prices of these inks significantly in the very near future (Feiyang Chen et al., 2020).

CHAPTER 3

GRAPHENE

Materials are the main forerunner of humankind for development and invention of new materials is essential for progress. Carbon based materials are the richest resources of earth and plays an important role on the evolution of human civilization. Carbon forms basis of organic chemistry for our planet and due to the presence of several bonding possibilities, carbon-based systems show many different structures and physical properties.

Existence of an element in crystalline solid state in at least two different forms which may differ in arrangement or bonding of atoms is called as allotropy. Hybridization or bond types of carbon valence electrons determine allotropes of carbon and elementary carbon has many allotropes. Carbon valence electrons can have the states of sp^3 or sp^2 hybridization of valence electrons. Elemental carbon exists in two natural forms which are diamond and graphite. Carbon with sp type of hybridization corresponds to diamond and the is the most well-known allotrope of carbon. In diamond four carbon atom links with strong covalent bonds and has three-dimensional face-centered cubic crystal structure (FCC) system lattice arrangement. Graphite has three-dimensional layered structure and well known to humankind after invention of pencil. Graphite has sp^2 type of carbon hybridization. Allotropes of carbon has different physical and chemical properties. Graphite for example is soft and conductive while diamond is hard and an insulator to electricity (Heimann et al., 1998).

Graphene is the basic building block of other carbon allotropes like graphite, carbon nanotubes and fullerenes. Graphene is formed from a layer of hexagon structure where carbon atoms are packed densely with two dimensional sp^2 bonded atoms in honeycomb crystal lattice. Length of sp^2 bond is about 0.142 nm and interplanar distance is 0.33 nm when sheets are stacked upon each other. Figure 2. shows representation of graphite and graphene structures.

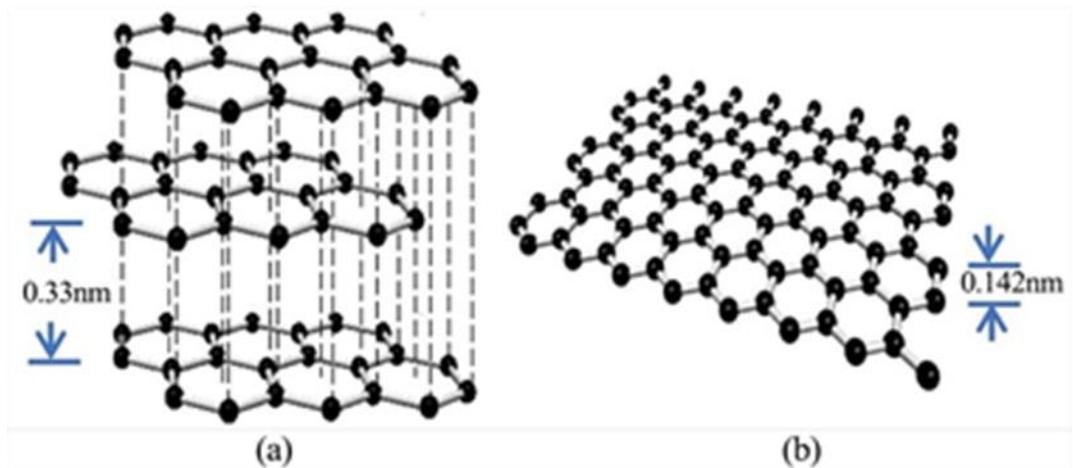


Figure 2. Presentation of structures of a) Graphite b) Graphene.

(Source: Heimann et al., 1998)

Graphene was firstly isolated in 2004 by Andre Geim and Konstantin Novoselov with mechanical exfoliation of pyrolytic graphite. This study led them to receive Nobel Prize in Physics in 2010. Before this study scientists believed that graphene like materials could not be distinguished independently due to stability problems. Significance of graphene is increasing steadily due to its unique properties and the increase in the number of publications by Scopus database (until 30 June 2019) is shown in Figure 3.

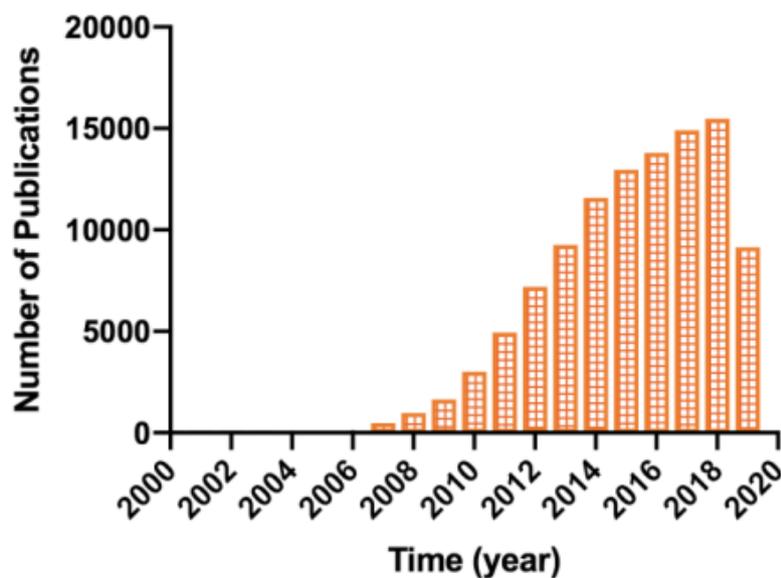


Figure 3. Change of “Graphene” word containing papers in title yearly.

(Source: Zhang et al., 2019)

3.1. Graphene Properties

Popularity of graphene research arose from extraordinary properties of graphene. Single layered graphene has surface area of 2600 m²/g, large thermal conductivity 3000-5000 W/(mK) and this thermal conductivity enhance importance of graphene in thermal conductivity materials. Room temperature charge carrier mobilities (μ) which exceeds 15000 cm²/(Vs) (Raju et al., 2017). High electron mobility in graphene provide accessibility to quantum Hall effect. Graphene has a temperature independent behaviour between 10 K to 100 K. For indeed and annealed graphene materials mobility was reached up to 200,000 cm²/(Vs) which is highest reported value for a semiconductor (Morozov et al., 2007). Graphene like other carbon allotropes show excellent mechanical properties. Tensile strength of graphene was found 130 GPa (Phiri et al., 2017).

Graphene is defined as zero band gap semiconductor and has very high electrical conductivity due to meeting of Dirac point by valence bonds. Carbon atoms have six electrons of which two is located in the inner Shell and four in the outer shell. This means four electrons in the outer Shell can form four bonds however in graphene one carbon atom bonded to three other due to sp² hybridization. This provides one electron which can easily involve in electric conduction. This property of graphene generates a chance for its use in semiconductor industry for the development of new devices. All these unique properties of graphene resulted in calling this material as “miracle material” in material science world (Bharech & Kumar, 2015).

Unique properties of graphene such as high carrier mobility, large surface area and high thermal conductivity places graphene to be a good candidate raw material in the production of conductive inks. Until now graphene based conductive inks were used in many applications such as sensors, conductive polymers, and supercapacitors.

3.2. Graphene Production

Graphene can be produced by the bottom-up (construction) and the top-down (destruction) techniques and these synthesis techniques are schematically shown in Figure 4. The bottom-up technique uses growing up graphene on various substrates. The bottom-up methods include chemical vapor deposition (CVD), epitaxial growth, substrate-free

gas-phase synthesis (SFGP), template route and total organic synthesis. Bottom-up methods can produce almost defect free graphene layers which also has high production costs and sophisticated production set-ups are main drawbacks for these methods. Top-down methods such as mechanical exfoliation, arc discharge, oxidative exfoliation-reduction, liquid-phase exfoliation (LPE) and unzipping of CNT involves production of graphene from bulk carbon sources (graphite) with isolation of graphene. Generally, top-down methods are easily scalable and produce high quality graphene but have some consistency and low yield problems. Bottom-up and top-down methods are shown in Figure 5. (Jiat et al., 2019).

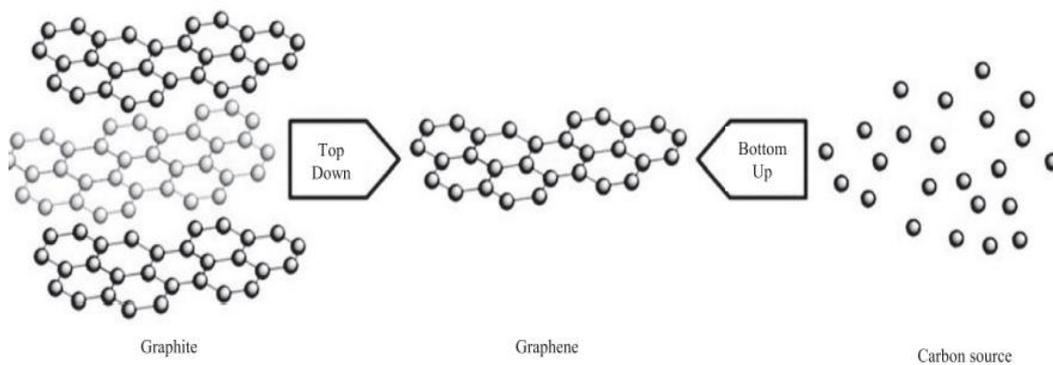


Figure 4. Graphene synthesis methods.

(Source: Jiat et al., 2019)

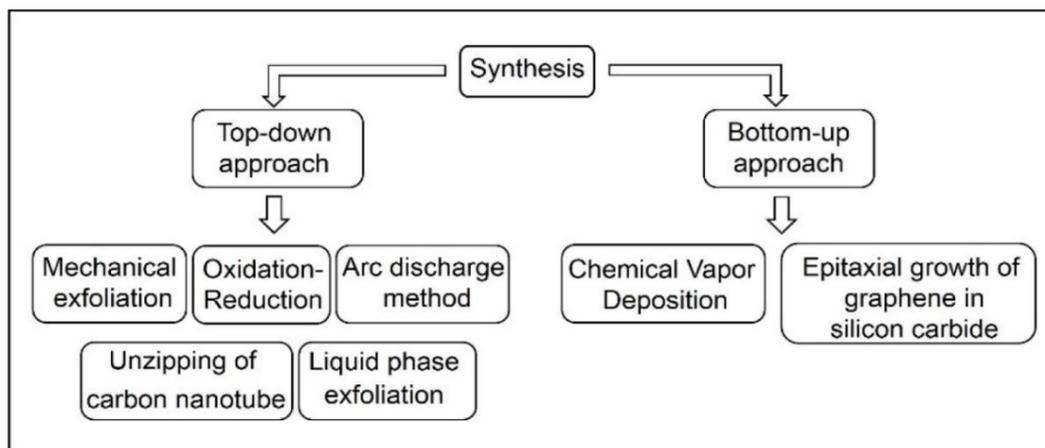


Figure 5. Top-down and Bottom-up approaches for graphene synthesis.

(Source: Santhiran, et al., 2021)

3.2.1 Top-Down Methods

Wan-der Waals forces hold graphene layers together. High purity graphene layers can be formed if higher stresses than Wan-der Walls forces are applied to the material. Mechanical stress is applied to graphite material to destroy these attractive forces between graphene layers in mechanical exfoliation. The most common techniques for mechanical exfoliation are sonication, high shear mixing and ball milling. The importance of shear force-based methods like ball-milling for graphene production is increasing. Quality of graphene production with ball milling is managed with parameters of grinding medium type, time, and chemical additive materials (Santhiran, et al., 2021).

Cutting carbon nanotubes in axial or longitudinal direction to single or few layered graphene constitutes another alternative method which necessitates high strains ($10^{8-10}/s$) to break the link between C-C atoms. Several methods such as chemical attack (treatment with H_2SO_4 and oxidation with KMn_4) (Kosynkin et al., 2009) plasma etching, metal catalyst etching was also proposed but these methods require expensive chemicals. In arch discharge method high electrical current is applied in the reaction chamber to create high temperatures up to $3727-5727$ °C under an inert environment. The use of electricity and inert environment increases the cost of graphene production through this method significantly.

3.2.1.1 Liquid Phase Exfoliation

Liquid phase exfoliation (LPE) is one of the common methods employed in the production of single or few layered graphene. Liquid phase graphene dispersion could be divided into two parts which are graphene exfoliation and graphene dispersion. Liquid phase exfoliation of graphene is achieved by the separation of multilayered graphite structure into single or few layered graphene structure by overcoming Wan der Walls forces where the selection of a proper solvent is critical. Surface energy, tension, Hansen-Hildebrand solubility parameters are important in the selection of solvents in LPE. Liquid phase exfoliation has many advantages compared to solid phase and gas phase methods due to its better processibility, lower cost, shorter production durations and the possibility of an easy application in large scale production. Ultrasonic treatment, mechanical exfoliation and electrochemical exfoliation are main liquid phase exfoliation

methods. Natural flake graphite is used in liquid phase exfoliation as a raw material. Graphite is intercalated to have an expanded graphite initially for overcoming Wan der Walls forces between layers by the following steps in this method. Dispersion process of graphene is schematically (Li et al., 2019) shown in Figure 6.. Ultrasonic degradation also has the advantage of low cost and operation simplicity while the adaptation to industrial scale production can be stated as the main drawback. Mechanical LPE method includes shearing and ball milling. Table 1. shows comparison of chemical properties, advantages and issues of common solvents used for exfoliation of graphite (Htwe et al., 2022).

Table 1. Comparison of chemical properties, advantages, and issues of common solvents for graphite conductive inks exfoliation. (Source: Htwe et al., 2022)

Name	Boiling Point	Formula	Advantages	Issues
DMF	153	C ₃ H ₇ NO	Good dispersion High stability	Restricted to be used with plastic substrate, Expensive, Highly toxic, hazardous
NMP	202	C ₅ H ₉ NO		
DMSO	189	C ₂ H ₆ OS		
Tetrahydrofuran (THF)	66	C ₄ H ₈ O	Less toxic Low cost	Poor graphene dispersion, require adding stabilizer
2-propanol (IPA)	83	C ₃ H ₈ O		
Toluene	111	C ₇ H ₈		
Acetone	56	C ₃ H ₆ O		

(cont. on next page)

Table 1. (cont.)

Name	Boiling Point	Formula	Advantages	Issues
Cyclohexanol	162	C ₂ H ₁₂ O	Less toxic Low cost	Poor graphene dispersion, require adding stabilizer
Ethanol	78	C ₂ H ₆ O		
Water	100	H ₂ O	Non-toxic Low cost	Poor graphene dispersion Need surfactant to disperse Low stability Less wetting properties

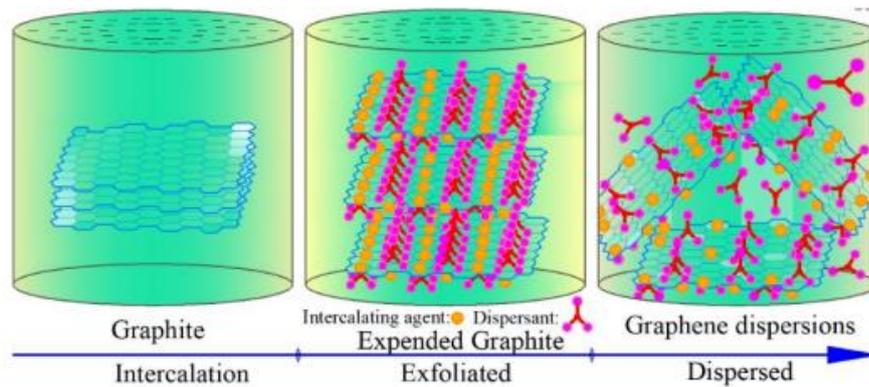


Figure 6. Graphene exfoliation and dispersion process.

(Source: Li et al., 2019)

3.2.2 Bottom-up Methods

Chemical Vapor Deposition (CVD) based methods depend on the decomposition of hydrocarbon gases at high temperatures (650–1000 °C) for the formation of graphene on metal substrate surfaces such as Cu and Ni. Carbon atoms dissolve in the metal substrate after hydrocarbon decomposition in the CVD reactor and the carbon solubility decreases during cooling. Carbon atoms diffuse out of the metal substrate and form graphene layers during the cooling stage. Figure 7. shows a typical CVD process. During that process metal substrate surface behave as a catalyst. CVD method can produce defect

free high quality graphene layers, but the main disadvantages of this method is high production cost and graphene transferring problems to other surfaces. Graphene can also be synthesized with epitaxial growth. This method depends on decomposition of silicon carbide under vacuum. Si atoms sublime at high temperatures in the 1200–1600 °C range and under high vacuum and only C atoms remain in the reaction site. Aggregation of C atoms form graphene layers (Zhang et al., 2012).

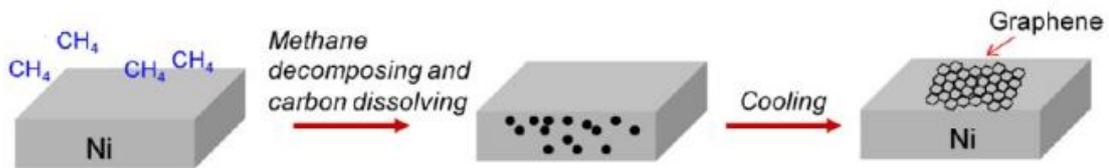


Figure 7. CVD Process.

(Source: Zhang et al., 2012)

3.2. Graphene Inks

There are two main routes for graphene use in conductive inks. The first route involves reduction of graphene oxide, and the other is accomplished by the exfoliation of graphene. First method requires harsh chemical treatment in concentrated hydrophilic functional groups and high post print temperatures. Printing of graphene-based materials are generally performed by liquid phase ink solutions. That's why top-down graphene-based ink production methods are preferable. Graphene based conductive inks must be stable to perform steady and uniform performances. Conductive inks must have well adhesion properties to printing surfaces (Jiat et al., 2019).

Carbon black pigments are generally produced from petrochemical products. Most of the studies on the use of carbon in conductive inks are concentrated on nanotubes, graphene, graphite, and carbon black. Electrical conductivity of graphite is a result of the layered structure and anisotropic chemical bonding between carbon atoms. Ten microns length of graphite particles are generally combined with sub-micron level carbon blacks to improve electron transfer between graphite plates due to high surface area. Combination of carbon black and graphite in polymeric binder increases conductivity

than individually usage of them in conductive inks. Carbon black particles which are smaller than graphene or graphite particles behave as energy carrier (Zhang et al., 2012).

Conductive inks with graphite to carbon black ratios of 0.5, 1, 1.8, 2.6 and 3.2 were prepared in vinyl polymer and screen printing was applied to investigate the effect of formulation on rheology and conductivity. Inks containing carbon contents of 29,4 and 21.7 wt% were called as lower and higher carbon contents. In formulation remaining amount was formed by resin dispersion. Inks containing higher carbon black content had higher viscosities within the range of 1 s^{-1} and 200 s^{-1} because of lower particle size and higher surface area of carbon black than graphite. Inks with higher carbon contents had higher conductivity at graphite to carbon black ratio of 2.6 with resistivity of $0.029\ \Omega\ \text{cm}$. Lower carbon containing inks had higher resistances due to lower thicknesses of printings. Lowest resistivity for these inks was measured at graphite to carbon black ratio of 1.8 with resistivity of $0.04\ \Omega\ \text{cm}$ (Phillips et al., 2017).

Aqueous dispersions of graphene sheets and carbon black were prepared with ball milling method in a recent work (Yang et al., 2020). Ink preparation and milling was achieved with 5-10 mm diameter zirconia balls. Screen printing was used for printing of patterns. After screen printing sandwich like structure was observed in the SEM images and graphene sheet use lowered the settling possibility of dispersion prepared with only carbon black. Rheological properties of inks prepared with various carbon black/graphene sheets were determined and all samples had a shear thinning behaviour. Dynamic rheological properties were also determined by determining initially linear viscoelastic region was conducted with strain amplitude sweep test. Frequency seep test measurements was conducted at 0.05 % and G' was determined to be higher than G'' which showed a solid-like behaviour. G' and viscosity of inks increased with higher graphene sheet content. The SEM images have shown that the graphene sheets created bridges between carbon black agglomerates. Increase of graphene content to 10 % formed a well-dispersed network. Mixture of graphene and carbon black in ink provided plane to point contact between particles which also increased potential electron transfer pathways. Further increase of graphene content to 15% resulted in the formation of gaps due to insufficient carbon black content to fill the gaps between graphene overlapping. Graphene content effect on resistivity of printing was also measured with four points probe method. Increasing graphene content from 0 wt% to 10 wt% decreased resistivity but further increase of graphene content to 15 wt% resulted in higher resistivity. Likely reason of this behavior was explained with formation of gaps by graphene overlapping due to relative

low carbon black content. Lowest resistivity was measured for the 10 wt% graphene containing ink with a resistivity of $0.23 \pm 0.01 \Omega \text{ cm}$ (Yang et al., 2020).

Carbon particles which are graphite (size < 20 μm) and carbon black (size SEM 45 nm), polymer resin and solvent effect on conductive ink performance were investigated. Ethyl cellulose (EC) and polyvinylpyrrolidone (PVP) was selected as main resins and dissolved in diethylene glycol ether, 4-Hydroxy-4-methyl -2-pentanone (HMP) and ethyl alcohol. Prepared samples were applied on substrate with screen printing method. All ink samples containing 20 wt% graphite and carbon black at different ratios had shear thinning behavior and their viscosity decreased with increasing shear rate. Viscosities at shear rates of 200 s^{-1} , 500 s^{-1} , 1000 s^{-1} were compared, and higher viscosities were measured for inks with higher carbon black content which showed particle size distribution effect on viscosity. Presence of graphite particles with higher particle sizes were assumed to be the stabilized carbon black particles. Polymeric binder ratio and total carbon ratio increase resulted in higher viscosities with noticeable shear thinning effect. Replacement of diethylene glycol butyl ether with HMP had no significant effect on viscosity and thixotropy. On the other hand, viscosity measurements of ethyl alcohol containing samples couldn't be completed due to the fast evaporation with irreproducible results. Increase of total graphite, carbon black content from 15 to 35 wt% resulted in lower sheet resistance values and lowest sheet resistance was measured as $32.4 \Omega \text{ sq}^{-1}$. Higher EC resin concentration decreased sheet resistance due to optimal dispersion process and particle size distribution. Effect of solvents with different boiling points did not have significant effects on sheet and volume resistance (Hatala et al., 2018).

Ball milling method was used to prepare extremely conductive graphene nanoplatelet (GNP) inks from graphite to coat several surfaces. DY50 was used as modifier which provides both dispersion efficiency and restacking after printing. Sheet resistances of inks printed on films were measured with four-point method. Increasing dip coating cycle from 1 to 6 on the surface of PET films decreased sheet resistance from 750 U/sq to 28 U/sq (Zhang et al, 2017).

Screen printing inks with graphite nanoplates (GNP) were prepared with combination of shear and ultrasonication exfoliation methods in mixed isopropanol (IPA)- water medium. Most of the exfoliated GNP flakes had lateral sizes of 2–4 μm . GNP conductivity under shear mixing (2h) showed only small increase. Noticeable conductivity increase was observed after 2 h shear mixing and 4 hours bath sonication. According to SEM images, increasing processing time to 6 and 12 h resulted in decrease

in voids and unexfoliated graphite flakes were very thick. Sheet resistance of printed graphene ink was measured as $0.875 \Omega/\text{sq}$. The ink had shear thinning behavior which was interpreted as suitable for screen printing (Leng, et al., 2019).

Screen printing graphene conductive ink was produced with jet cavitation liquid phase exfoliation. Carbon black was added to graphene ink to increase conductivity. Rheological properties were important to print defect free patterns and steady state rheological properties were measured between range of $0.1\text{--}1000 \text{ s}^{-1}$. All inks behaved as pseudoplastic fluid. At high shear rates, 1000 s^{-1} , carbon black free ink had the higher viscosity at high shear rates. For 15 % carbon black containing dispersions, ink containing thinner and larger area of graphene flakes had higher viscosities. Rheological behavior during screen printing was examined at three different stages which simulated loading, printing, and recovery on substrate of screen printing. Elasticity of inks were compared with ratios of viscosities at 3rd and 2nd stages. Higher ratio of viscosity at 3rd to 2nd stages was interpreted as having a higher elasticity and increase of carbon black ratio from 10 % to 20 % increased elasticity. Conductivity comparison of inks with different carbon black and graphene were also conducted. Increase of carbon black ratio to 15 % of total fillers increased conductivity 8-14 times compared to inks containing only graphene as filler. Enhancement of conductivity of printed patterns with carbon black was investigated with scanning electron microscope and are shown in Figure 8. Surfaces of the graphene flakes and voids were fully covered with polymer and as shown in Figure 8a. This fully covering of surfaces resulted in poor contact between graphene flakes and conductivity were measured as $2.6 \times 10^3 \text{ S/m}$ and $1.1 \times 10^3 \text{ S/m}$ which are relatively low. The SEM image of the coatings prepared by the addition of 10, 15, 20% carbon black to graphene dispersion is shown in Figures 4 b, c, d respectively. Figure b and Figure c shows carbon black distributions located at the edges of graphene flakes. This situation created increased conductive filler around graphene flakes and increased conductivity. Further increase of carbon black content to 20% damaged dispersion performance of fine particles and created some agglomerates which also decreased conductivity by increasing gap between graphene particles (Liu et al., 2021).

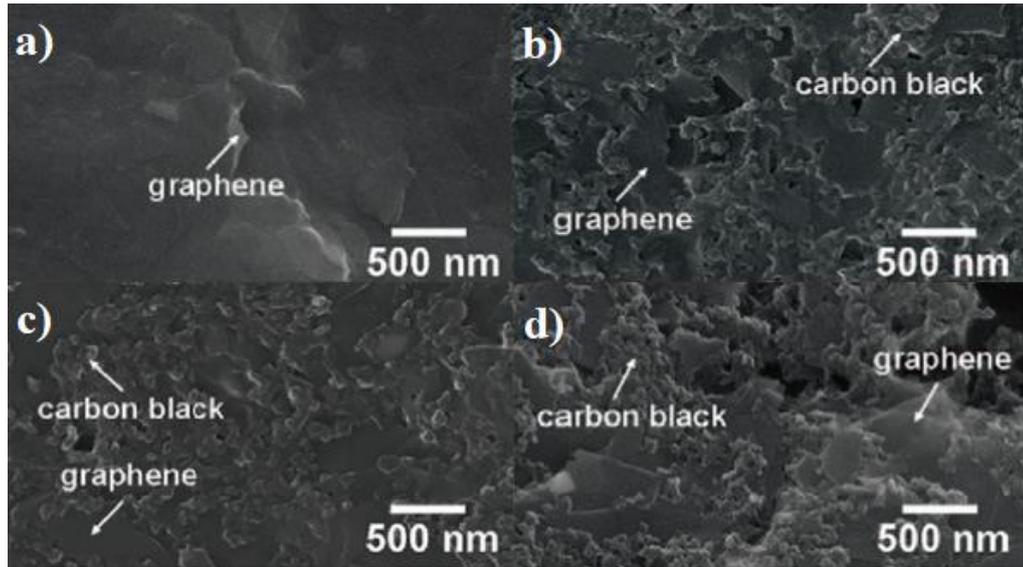


Figure 8. Highly conductive graphene/carbon black screen-printing inks for flexible electronics. (Source: Liu et al., 2021)

Few layered ~160 nm graphene flakes were synthesized from graphite with liquid phase shear exfoliation due to faster and scalable production of this method. Exfoliation efficiency was followed with graphene flake diameter and thickness in three organic solvents which are Ethanol, N- dimethylformamide, N-Methyl-2-pyrrolidone. Shear mixing and time was varied to optimize thickness and diameter of graphene particles. Solvent was found as a critical factor in effecting particle diameter and thickness. Stable and concentrated (3.2 mg/mL) graphene ink was produced with that method. Printed transparent conductive films with graphene had conductivity of 4×10^4 S/m with sheet resistance of $260 \Omega/\text{cm}$ (Majee et al., 2016). Table 2. compares some studies prepared with different solvent types and compares their resistances.

Table 2. Summary of previous studies on solvent-based graphene conductive inks.

Solvent	Printing Method	Substrate	Resistance	Source
NMP	Inkjet	Si/SiO ₂	$30 \text{ k}\Omega^{-1}$	(Htwe et al., 2022)
Ethylene glycol	Inkjet	FS3 paper	1-2 $\text{k}\Omega/\text{sq}$	(Htwe et al., 2022)

(cont. on next page)

Table 2. (cont.)

Solvent	Printing Method	Substrate	Resistance	Source
Ethanol/DMF/NMP	Inkjet	Glass/PET	260 Ω /sq	(Htwe et al., 2022)
Terpineol/ethanol	Aerosol-jet	PET	470 \pm 80 Ω /sq	(Htwe et al., 2022)
Ethylene glycol	Screen	PET	34.1 Ωm^{-1}	(Htwe et al., 2022)
Water	Inkjet	Glass	43 Ω	(Kirova et al., 2019)
Water	Inkjet	PETG	20 Ω	(Kirova et al., 2019)
Water	Inkjet	Acrylic	23 Ω	(Kirova et al., 2019)
Diacetone alcohol	Screen	PET	10 k Ω	(Phillips et al., 2017)

CHAPTER 5

EXPERIMENTAL STUDY

This chapter introduces the materials, exfoliation of graphite, dispersion preparation, conductivity measurement methods, ink viscosity and rheological behavior characterization procedure, particle size measurement, and optical microscope characterization. Exfoliation of graphite and preparation of concentrated dispersion of carbon black pigment with graphite in solvent-borne medium was conducted in the first step of conductive ink layer formation. Prepared inks were printed on paper and measurement of the dried coating resistances were conducted in the second step. Different exfoliation liquids and graphite/carbon black ratios were used in the formulation of inks and their effects on the resistance of the layers were finally investigated. Figure 9. shows a sample of one of the prepared inks.



Figure 9. Picture of ink.

5.1. Materials

Graphite was used to provide electrical conductivity to the ink. Graphite was received from Molchem which was reported to have an average particle size of 44 μm and %99 purity by the company. Graphite was used to produce a total of 10 batches of carbon inks with graphite/carbon black ratios of 0.5, 0.75, 1, 1.5 and 2.

Carbon black was used for dispersion preparation was supplied by Orion Engineered Carbons. This pigment was reported to have an average particle size of 31 nm and BET (surface area) of 62 m^2/g according to the manufacturer. Pigment content of dispersions varied between 20 wt% and 30 wt%.

Liquid phase exfoliation was conducted with four different solvents. NMP, DMF, water, and ethylene glycol were used in this work.

Graphite, carbon black pigment, exfoliation liquid solvent, and varnish were coded as G, CB, EL, S and V respectively. The numbers at the beginning of codes showed weight ratios present in dispersions.

5.2. Exfoliation of Graphite

Exfoliation of graphite were conducted by using liquid ball milling. A mixture of liquid and graphite powder were placed in the grinding jar of the mill (Retch PM 100) with zirconium oxide balls a mixture of 5 mm and 10 mm diameter balls. The grinding jar was placed on the rotating tray of a planetary mill. Carbon powder mixtures with four different carbon/graphite ratios and four different liquids were ground for 4 h rotation duration at a rotation speed of 400 RPM.

5.3. Dispersion (Ink) Preparation

Dispersions were prepared using high speed mixer and a dispersion cup. Dispersion process was divided into three main parts which were pre-mixing, milling and let-down. High speed mixer was used for both premixing and milling stages. Predetermined amounts of varnish, solvent, and carbon black was placed in the dispersion cup along with the exfoliated graphite/carbon black/exfoliation liquid slurry. In pre-

mixing stage, graphite slurry, carbon black, solvent and varnish were mixed at 5100 Rpm without beads for 30 minutes. Effective wetting of pigment particles was the purpose of pre-mixing stage, and same ratios were used for all samples to prevent deviations due to wetting stage. Beads were added to the dispersion cup after premixing, and dispersions were ground during one hour with 5100 Rpm. Glass beads with sizes of 1.3 mm were used for regular dispersions. Weight ratio of bead to ink slurry mixture was 2:1 to achieve effective dispersion. Dispersion and beads were separated by using 100-micron sieve after milling. Remaining parts of the formulations were added to complete formulation to 100 wt% during the let-down process. There was no cooling jacket present around the dispersion cup which may be the reason for some solvent evaporation/loss during pre-mixing and milling stages. This evaporated amount was added to samples at the end of the let-down process. Prepared dispersion (ink) samples are shown in Table 3. and schematic representation of ink preparation steps are shown in Figure 10.. Totally 9 different samples were prepared.

Table 3. Prepared inks.

	EL	EL (% wt)	G (% wt)	CB (% wt)	G/CB	V (% wt)	S (% wt)
Exfoliation Liquid Effect	Water	10	10	10	1	35	35
	Ethylene Glycol	10	10	10	1	35	35
	DMF	10	10	10	1	35	35
	NMP	10	10	10	1	35	35
G/CB Effect	Ethylene Glycol	12.5	8.33	16.67	0.5	31.25	31.25
	Ethylene Glycol	12.5	10.7	14.3	0.75	31.25	31.25

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Table 3. (cont.)

	EL	EL (% wt)	G (% wt)	CB (% wt)	G/CB	V (% wt)	S (% wt)
G/CB Effect	Ethylene Glycol	12.5	12.5	12.5	1	31.25	31.25
	Ethylene Glycol	12.5	15	10	1.5	31.25	31.25
	Ethylene Glycol	12.5	16.67	8.33	2	31.25	31.25

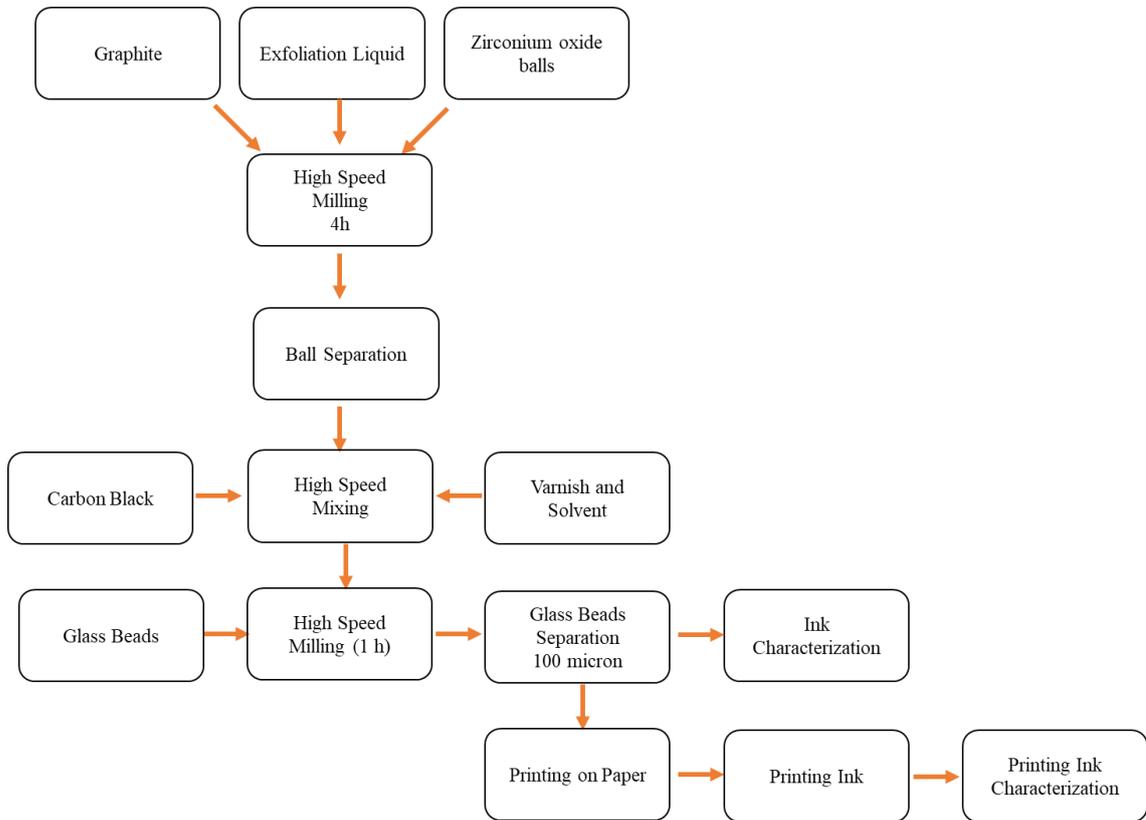


Figure 10. Schematic representation of ink preparation steps.

5.4. Printing and Resistance Measurement

Printing was carried out on a Leneta Applicator Charts which is 14 mil thick. Leneta is sealed with a 100% solids clear UV topcoat which prevents applied coatings from penetrating into the paper. The paper contains no optical brighteners which can affect instrumental color measurements. 30-micron ink stick bar was used for the preparation of a specific film thickness.

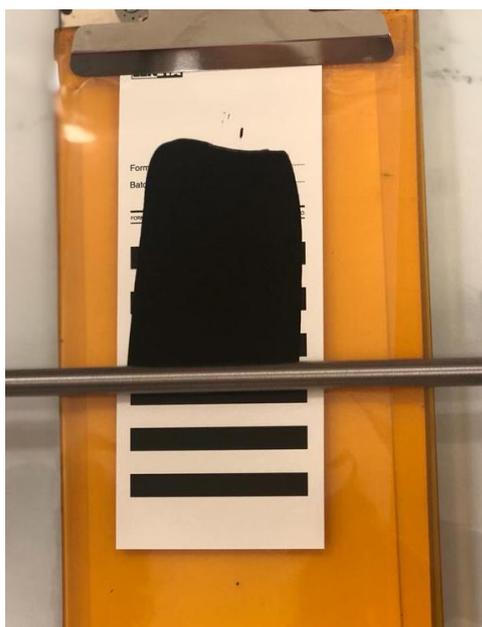


Figure 11. Picture of printed ink.

The print image included a series of 100 mm long lines of differing widths and a 50 mm square solid patch for sheet resistance assessment. Printed samples were dried in a box oven at 40°C for 30 min and left overnight before measurement.

Resistance of printed samples was measured using Uni-T Ut 61E digital multimeter in two-point mode.

The print image included a series of 100 mm long lines of differing widths and a 50 mm square solid patch for sheet resistance assessment.

5.5. Viscosity Measurement

Rheological measurements were done with Haake Mars II Advanced Rheometer using the plate-plate sensor of PP35Ti. Rheological behavior of dispersions was

determined by both steady shear and dynamic shear measurements. Measurements were done at 20 °C and gap size between plates was adjusted to 1 mm. Before dynamic shear measurements, pre-shearing wasn't applied, only samples were shaken in small jar, to prevent evaporation of solvent.

5.4. Particle Size Measurement

Particle size measurements were performed with Malvern Mastersizer 3000, which depends on dynamic light scattering (DLS). Before starting measurement, 5 drops of ink were added to 10 ml of ethanol solvent and mixed. This operation was done due to stay in obscuration range of particle size analyzer. Obscuration range was adjusted between % 4 and % 8 to prevent multiple scattering. After that, diluted sample was added to dispersion chamber and particle size measurements were done. During that measurement, rotation speed was adjusted to 1600 rpm.

5.5. SEM and XRD Analysis of Powders and Films

The phase structure analysis of the graphite, carbon black, and exfoliated graphite was conducted by using Philips X'pert Pro XRD equipment. The morphological characterization of the powders in film fracture surfaces were conducted by using (SEM) FEI Quanta 250 FEG (Oregon, USA).

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Phase and Morphological Characterization of the Powders

The crystal structure of the graphite and the exfoliated graphite were analyzed by conducting X-ray diffraction (XRD) studies. Figure 12. shows that there are two characteristic peaks in the XRD pattern of the graphite/exfoliated graphite located at about $2\theta = 27^\circ$ and $2\theta = 55^\circ$. The NMP exfoliated graphite exhibited almost the same diffraction peaks with the as received commercial graphite which indicated that graphite still retained the structure of carbon atoms or molecules however the intensities of the diffraction peaks were significantly lower. The most intense peak located at $2\theta = 27^\circ$ was broadened slightly which may be due to the presence of a small amount of graphene since the XRD pattern of graphene has a very broad peak located at about $2\theta = 25^\circ$. The XRD analysis indicated in summary that the peak intensity of graphite was decreased compared with that of the original graphite during exfoliation which may most likely be due to the increase in interlayer distances and graphite exfoliation to some extent. This is because the size of the exfoliated layers became smaller.

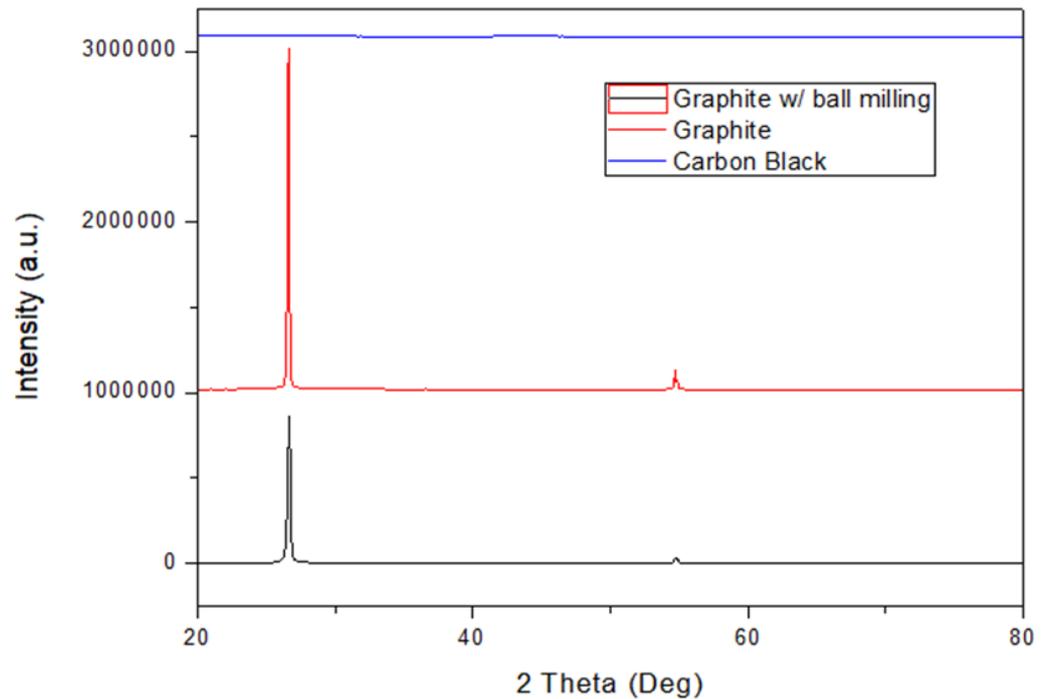


Figure 12. XRD patterns of the graphite, carbon black and the exfoliated graphite powders.

Scanning electron microscopy (SEM) images were taken for morphological investigation of the exfoliation effect on graphite. Figure 13. depicts morphologies and sizes of graphite, exfoliated graphite, and carbon black. Graphite and exfoliated graphite have irregular shaped flakey structure while carbon black shows a finer surface and nanometer sized equiaxed particles. It can be seen from Figure 13A, graphite's flake sizes are around 30-40 μm . Compared to graphite, exfoliated graphite's flake size decreased around 5-10 μm with overlapped morphological structure and is shown in Figure 13B. These images supported the fact that a significant level of exfoliation of graphite to smaller graphene sheet containing particles were accomplished during the ball milling process conducted in this work.

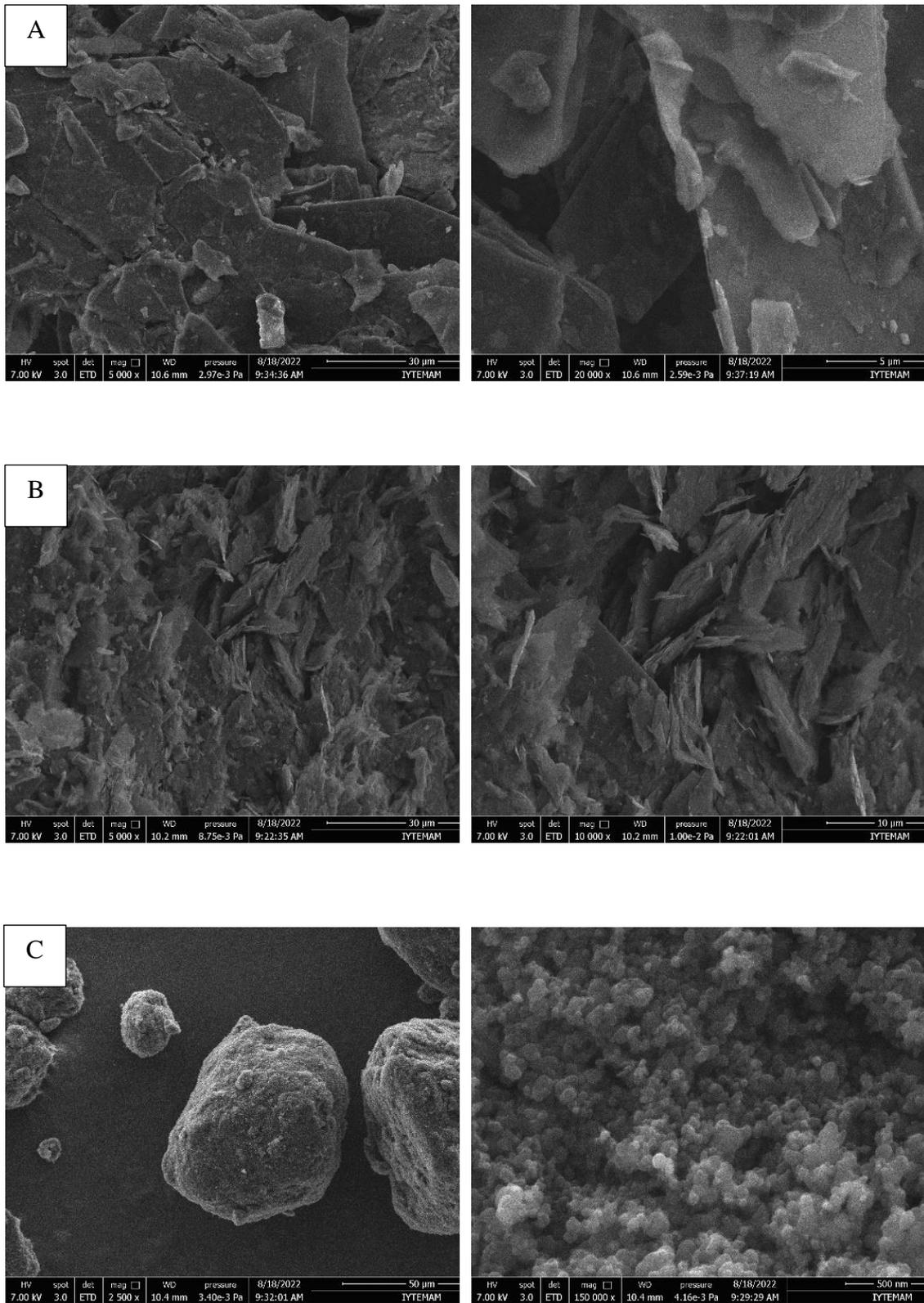


Figure 13. SEM graphs of (A) Graphite (B) Exfoliated graphite (C) Carbon black.

6.2. Exfoliation Liquid Effect on Graphene/Carbon Black Inks

6.2.1. Exfoliation Liquid Effect on Resistance

The electrical resistance of the inks with four different exfoliation liquids was investigated. Water, ethylene glycol, DMF and NMP were used as milling material. Molecular structures of the utilized exfoliation liquids are given in Figure 14.

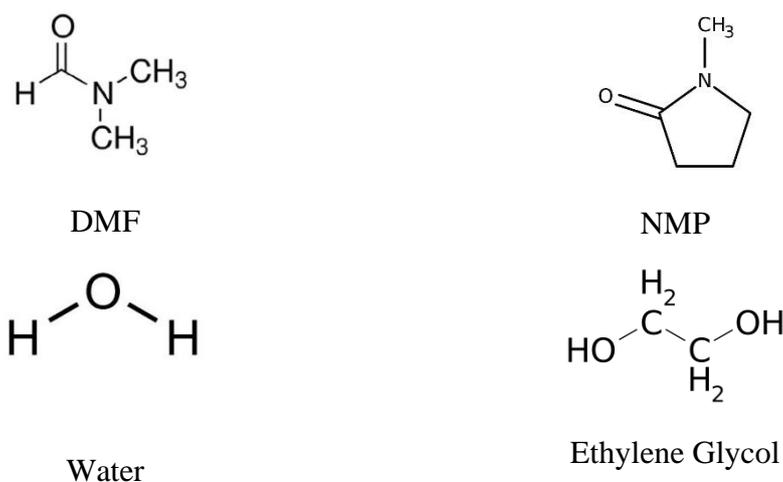


Figure 14. Molecular structure of different exfoliation liquid.

Exfoliation liquid effect on conductive ink resistance is shown in Figure 13. Maximum conductivity was obtained by using NMP exfoliation during ball milling (Resistance of 0.02 k Ω). DMF and ethylene glycol exfoliated ink layers gave slightly higher resistances of respectively 0.074 and 0.095 k Ω respectively. The highest resistance for these inks was achieved when water was used as the exfoliation liquid with a resistance of 1.40 k Ω which was about 70 times higher than the NMP exfoliated conductive layers. The reason for this finding may be stated as the presence of CH₃ and CH₂ groups in the molecular structure of the exfoliation liquids. The relatively low levels of exfoliation achieved by ball milling may be enhanced through chemical interactions compared with dominant hydrogen bonds present water was used as the exfoliation liquid.

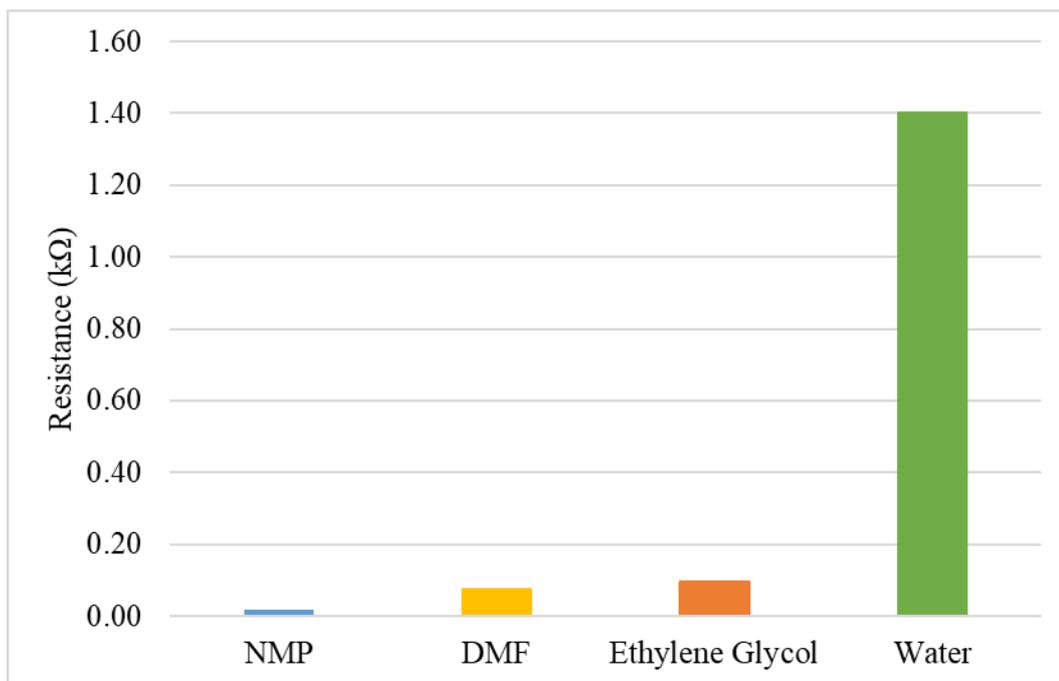


Figure 15. Resistance of the printed inks with different exfoliation liquid.

6.2.2. Exfoliation Liquid Effect on Particle Size

The particle size distributions of the inks prepared with identical total carbon contents and four different exfoliating liquids were determined for understanding the effect processing liquid on particle size reduction. Particle size distribution of the NMP, DMF; ethylene glycol and water exfoliated dispersions/inks are given in Figure 16. The NMP ink was found to have a bimodal particle size distribution with a larger volume percent of submicron particles. The average particle size of the NMP exfoliated ink was measured as 18.0 μm which also led to the preparation of conductive layers with the lowest resistance which will be discussed in the following sections. These results have shown that NMP was the best exfoliating liquid although water exfoliation caused a higher level of particle size reduction (a slightly higher submicron particle content and lower average particle size) as will be discussed later had a very high resistance. These results indicated that along with the particle size reduction (mainly of the graphite particles/phase) the packing of these graphite/carbon black particles during printing/drying plays a central role in determining the electrical properties/behavior of these conductive layers.

The average particle sizes of the samples prepared using DMF and ethylene glycol however were significantly higher and were determined as 28.6 and 38.4 μm respectively. It can be easily seen from the figure that although there are bimodal particle size distributions in all inks, the inks prepared by using DMF and ethylene glycol had a peak located around 100 μm while the sample with NMP had the similar large particle size located at about 20 microns with higher submicron particle content when compared with the organic exfoliation liquids. These findings support the fact that NMP exfoliated graphite better than the other two liquids providing a more favorable particle size distribution for consolidation/packing of particles during layer formation.

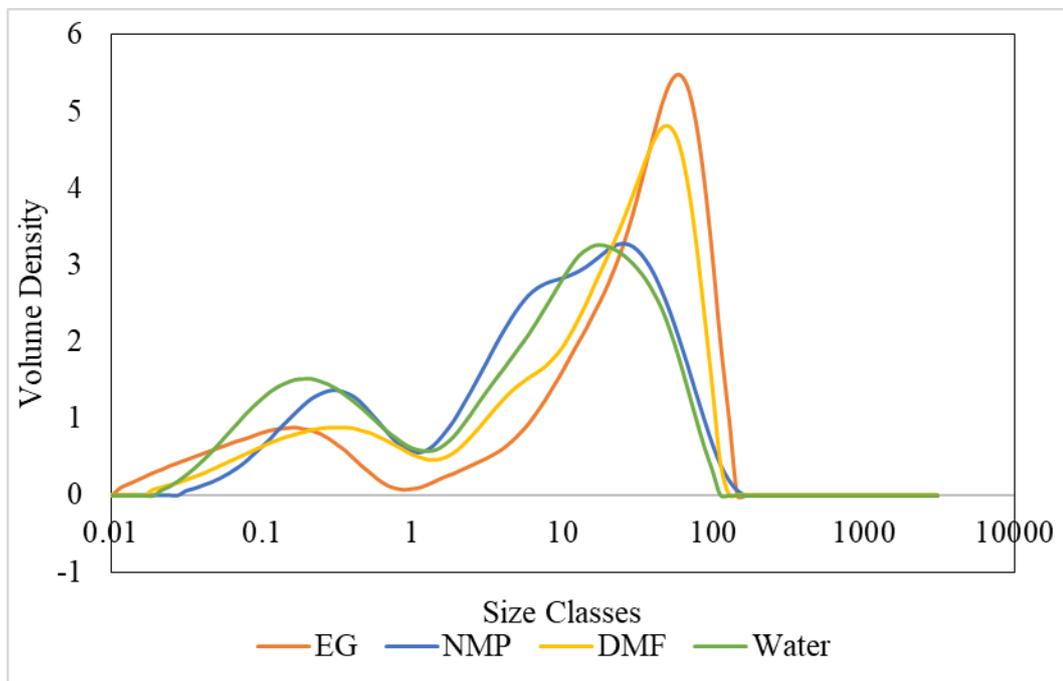


Figure 16. Particle size distribution of ink with different exfoliation liquid.

6.2.3. Exfoliation Liquid Effect on Viscosity

Rheological properties of inks are important for printing defect free conductive patterns. Exfoliation liquid effect on viscosity is shown in Figure 17. Viscosity of all inks decreased with increase in shear rate which showed a shear thinning behavior. Inks exfoliated with NMP had higher viscosities than other samples all over the range due to efficient exfoliation of graphite to graphene and smaller particle size distribution of inks. DMF exfoliated ink had the lowest viscosities which were close to the viscosities of EG

exfoliated ink. The viscosities of water exfoliated inks had higher viscosities than the EG and DMF exfoliated inks. The determined higher viscosity of water exfoliated/containing ink may be due to the incompatibility between the solvent-based resin and the remaining water in the ink. This incompatibility most probably formed large dispersion droplets in liquid medium and prevented flow of droplets over each other. In particle size measurements these droplets couldn't be determined due to the measurement at high rotation speeds (1600 rpm) during rheological measurements. This droplet formation could also explain higher resistance of water exfoliated inks.

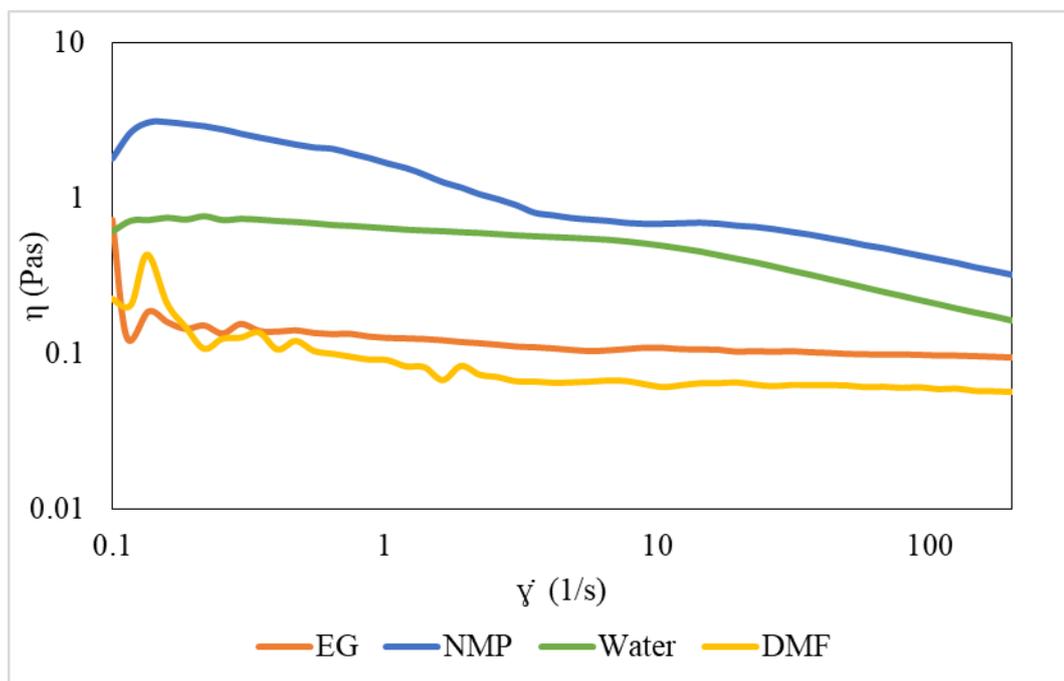


Figure 17. Exfoliation liquid effect on viscosity.

6.2.4. Exfoliation Liquid Effect on Thixotropy

Degree of thixotropy was determined by the area hysteresis loop test. In that test, thixotropic area was calculated from ascending and descending loops of shear rate curve. Ascending curve shows viscosity change with shear rate increase which forms upward curve for a thixotropic material. On the other side, descending curve shows viscosity behavior with shear rate decrease which depicts downward curve. Between shear rate increase (upward curve) and shear rate decrease (downward curve) any shear rate wasn't applied during 60 seconds.

Exfoliation liquid effect on thixotropy was investigated and shown in Figure 18. Highest thixotropic area which was $1801 \text{ Pa}\cdot\text{s}^{-1}$ was recorded for dispersion exfoliated with water and the highest thixotropy could be explained by incompatibility between resin and water. Thixotropic area of dispersion exfoliated with EG, NMP and DMF was measured as 50, 981 and $180 \text{ Pa}\cdot\text{s}^{-1}$ respectively. These results showed structure of water exfoliated conductive ink lately recovered back to initial condition. When thixotropy results are combined with resistance results, sample having the hugest thixotropy which is even above $1000 \text{ Pa}\cdot\text{s}^{-1}$ had the lowest conductivity.

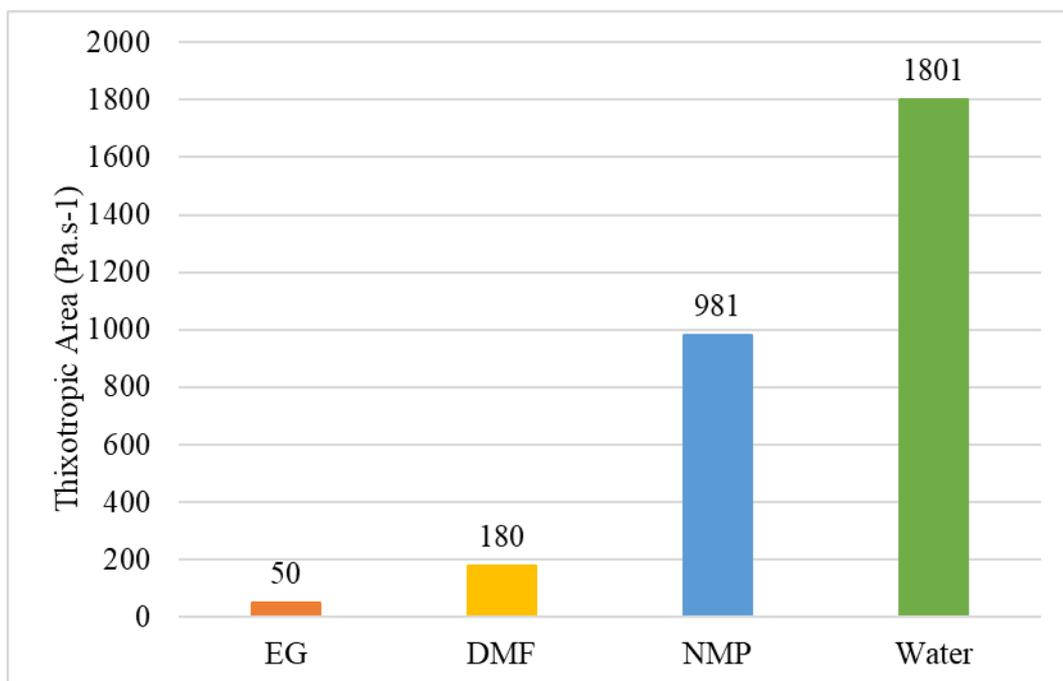


Figure 18. Exfoliation liquid effect on thixotropic behavior of conductive inks.

6.3. Effect of Graphite to Carbon Black Ratio on Conductive Inks

6.3.1. Effect of Graphite to Carbon Black on Resistance

Effect of graphite to carbon black ratio on the resistance of printed ink was investigated and is shown in Figure 19. For 25 wt % total carbon content inks, a graphite to carbon black ratios between 1 to 2 had higher conductivity than inks prepared at ratios lower than 1. Between these inks graphite to carbon black ratio of 1 containing had the lowest resistance of $0.045 \text{ k}\Omega$. When the graphite ratio was increased, without changing

the total carbon, from 0.5 to 1, the network structure formed by the graphite increased and its electrical conductivity improved. Increase in graphite content beyond the optimum loading, which is determined at G/CB ratio of 1 due to lowest resistance, resulted in higher resistances. A possible explanation for this is that, as the carbon black content is reduced, the polymer/carbon black matrix between the graphite particles has a lower carbon black concentration which makes it a relatively poor conductor. In addition, when a high percentage of graphite is used, sedimentation was observed. For this reason, when printing these samples, the graphite is not homogeneously distributed on the surface of paper and the electrical performance decreased.

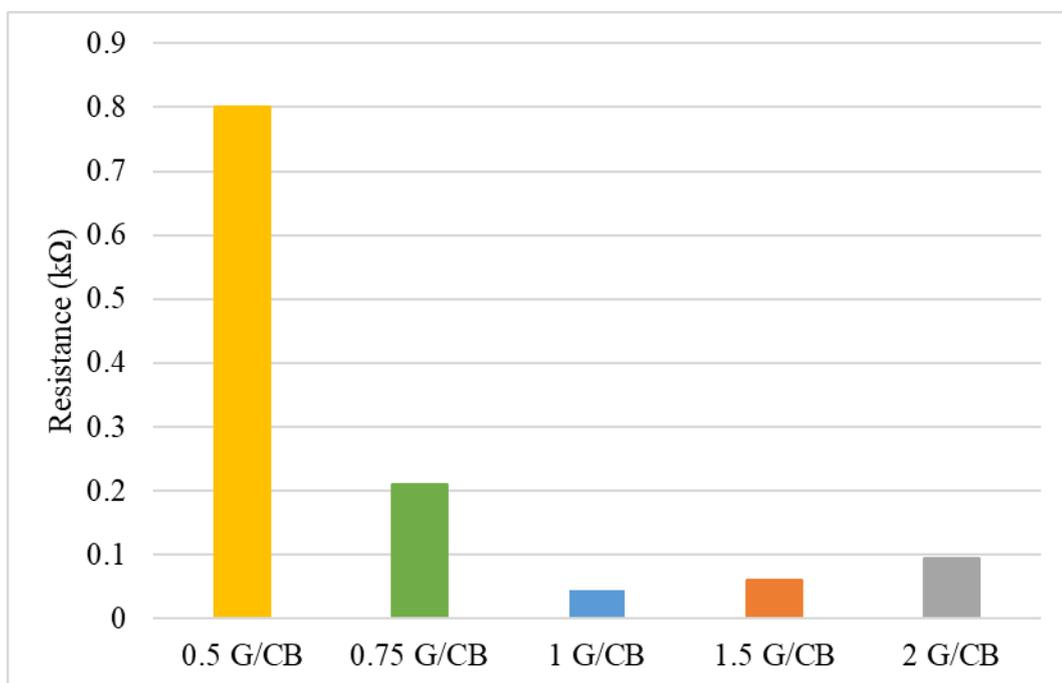


Figure 19. Resistance of the printed inks with 0.5, 0.75, 1, 1.5, and 2 mass ratios of graphite to carbon black

6.3.2. Effect of Graphite to Carbon Black on Particle Size

Particle size distributions of inks with graphite to carbon black ratio 0.5, 0.75, 1, 1.5 and 2 graphite are investigated to determine particle size effect on electrical conductivity and is shown in Figure 20. These samples were produced at same exfoliation and dispersion steps. As seen from figure, lowest particle size was determined at 0.5 ratio of graphite to carbon black because it already has a high CB content because graphite has

higher particle size than carbon black and it is more difficult to reduce the particle size. The electrical conductivity of sample with graphite to carbon black ratio of 0.5 was the lowest, graphite content was not enough to create a network with each other.

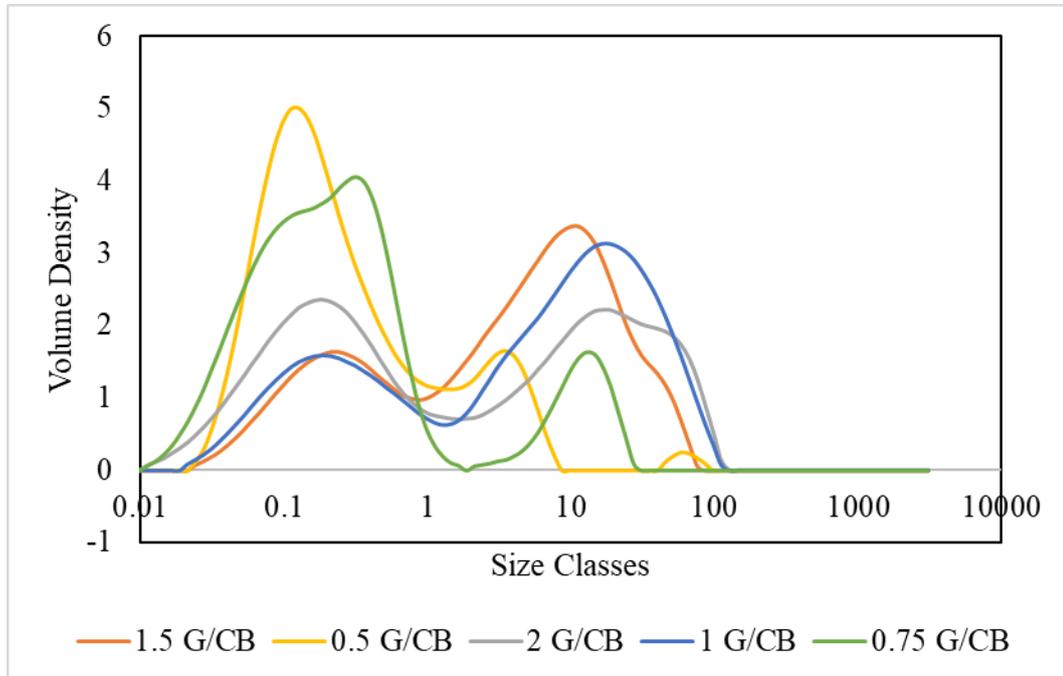


Figure 20. Particle size distributions of the printed inks with 0.5, 1, 1.8, 2.6 and 3.2 mass ratios of graphite to carbon black.

High carrier mobility of graphene improves electron transport between carbon black particles. Figure 21 (A). shows microscopic images of 0.5 G/CB containing ink, which carbon black particles connect to each other, and less graphene bridges found. Low graphene connection formation could be reason of high resistivity. Figure 21 (B). shows microscopic images of samples prepared with graphite to carbon black 1. As this figure shows primary connective network found between carbon black aggregate with help of graphene bridges. This structure could be reason of low resistance for that sample.

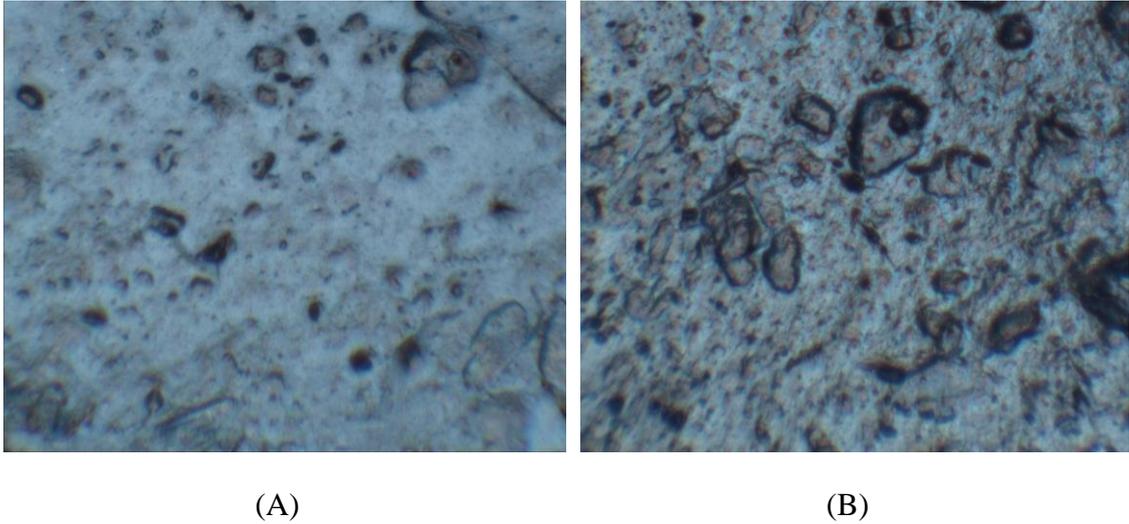


Figure 21. Microscope images of printed inks (A) and 0.5 parts graphite to carbon black (B) 1 parts graphite to carbon black.

6.3.3. Graphite to Carbon Black on Viscosity

Graphite/Carbon Black ratio effect on steady state rheological behavior of conductive inks were investigated in range of $0.1\text{--}100\text{ s}^{-1}$ and shown in Figure 22. Viscosity of all inks decreased with increase of shear rate which depicts shear thinning behavior. Viscosity of ink with 0.5 G/CB ratio was much higher than all other inks. The reason behind that situation could be related with excess amount of carbon black which have lower particle size and proved in particle size measurements. Viscosity of inks prepared with G/CB ratios of 1, 1.5 and 2 were measured close to each other. On the other hand, viscosity of ink with G/CB of 0.75 was measured lower than all other inks.

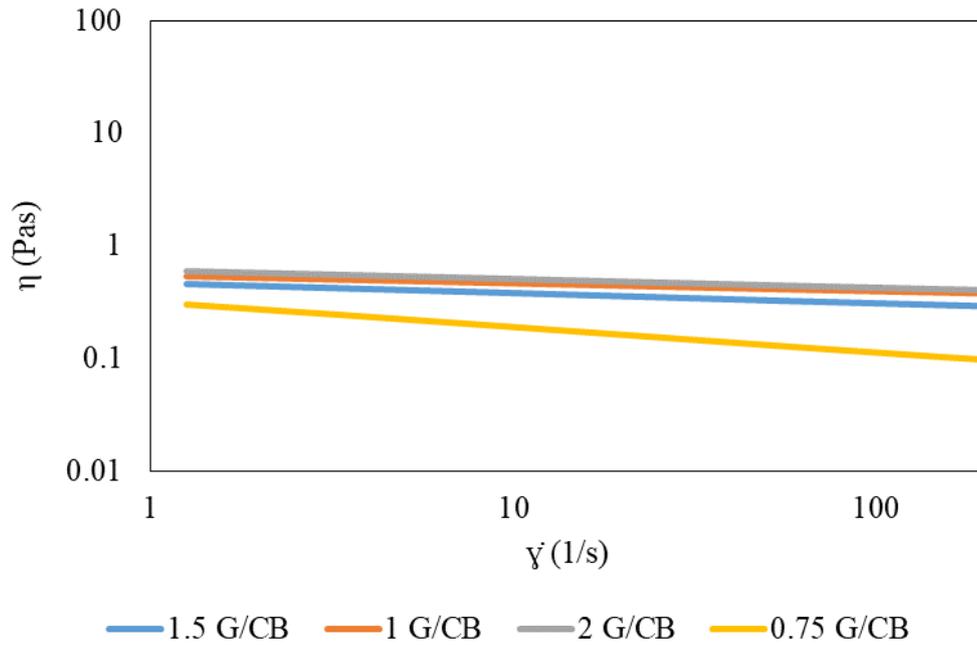


Figure 22. Viscosity-shear rate graph of inks with different G/CB ratios.

6.3.4. G/CB Ratio Effect on Thixotropy

Thixotropic behavior of conductive inks at G/CB ratios ranges from 0.5 to 2 was investigated and given in Figure 23. The highest degree of thixotropic behavior was measured at 0.5 G/CB ratio containing ink with value of $2430 \text{ Pa}\cdot\text{s}^{-1}$. Increase of finer CB particles in dispersion contributed to that highest thixotropy. Lowest thixotropy was measured at sample prepared with 0.75 G/CB ratio, the reason behind that situation could be sedimented or insufficient mix of carbon particles. Thixotropic areas for dispersion with G/CB ratios of 1, 1.5 and 2 was determined as 103, 114 and 44 $\text{Pa}\cdot\text{s}^{-1}$ respectively. As found in exfoliation liquid effect on resistance and thixotropy, sample largest thixotropy which is also above $1000 \text{ Pa}\cdot\text{s}^{-1}$ had the highest resistance.

Exfoliation liquid and graphite to carbon black effect on resistance of printed inks were investigated. At both investigation, samples having higher thixotropic areas than $1000 \text{ Pa}\cdot\text{s}^{-1}$ had highest resistance. Printing of an ink to paper surface divided into 3 sections which are, pouring on paper, printing and drying of ink. Thixotropic area also shows structural return back rate. Inks with high thixotropic behavior have longer structural return back rate (to initial structure) than evaporation rate. This situation could prevent effective structure formation between graphite and carbon black particles which

resulted in higher resistances. On the other hand, ink with lower thixotropy return to initial structure at the faster or same rate with drying of solvent and this situation increases formation of structures and decreases resistance.

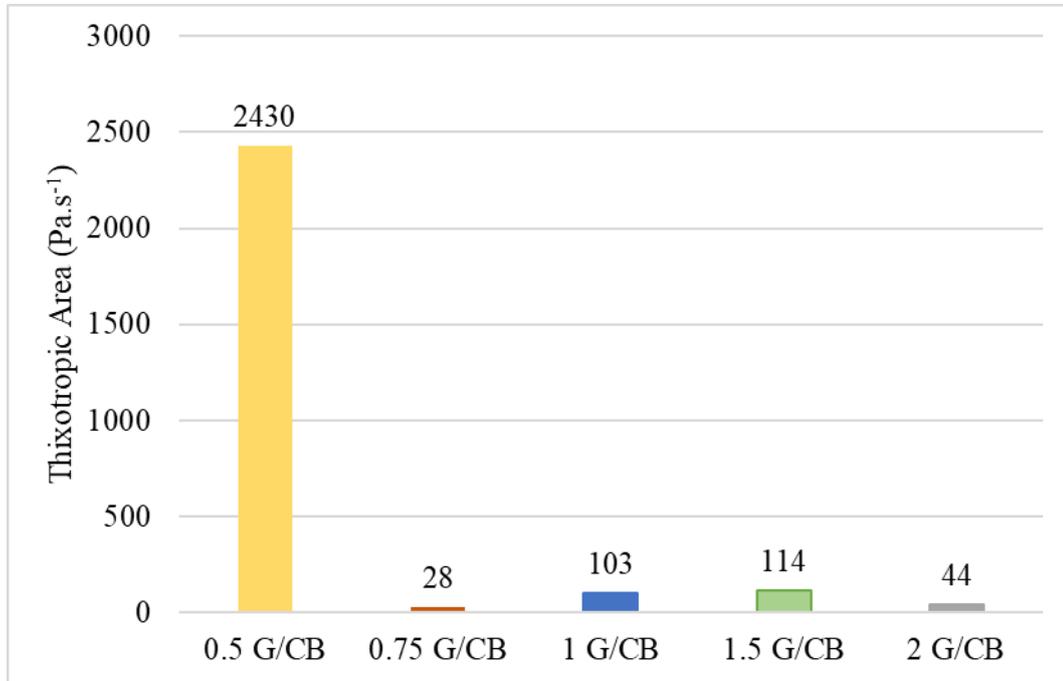


Figure 23. G/CB ratio effect on thixotropy.

6.4. SEM Analysis of Printed Conductive Films

Exfoliation liquid effect on graphite exfoliation and conductivity could be explained by SEM fracture surface topology of printed conductive inks and is shown in Figure 24. Conductive inks prepared with exfoliation of graphite with ethylene glycol had relatively large cracks on both the top and fracture surfaces as shown in Figure 24 (A). These cracks prevent interconnection between exfoliated graphite/graphene particles with significantly reduced sizes compared to the original particles which decreases the conductivity of the ink. SEM image of ink prepared by exfoliation of NMP is shown in Figure 24 (B). NMP exfoliated ink had lower/smaller cracks when compared the ink prepared by ethylene glycol exfoliated graphene. The top surfaces of the printed films were fully covered with nanometer sized carbon black particles. SEM image of DMF exfoliated graphene containing ink is shown in Figure 24 (C). and there is a uniform distribution between carbon black and graphene on the fracture surfaces with relatively

smaller cracks. The nature of the packing/consolidation of the two phases containing particles with significantly different size and morphology forms important differences between the microstructures. The differences in the mixing of the two phases is most likely responsible from the very high conductivities of the films prepared from NMP/DMF exfoliated graphite containing inks.

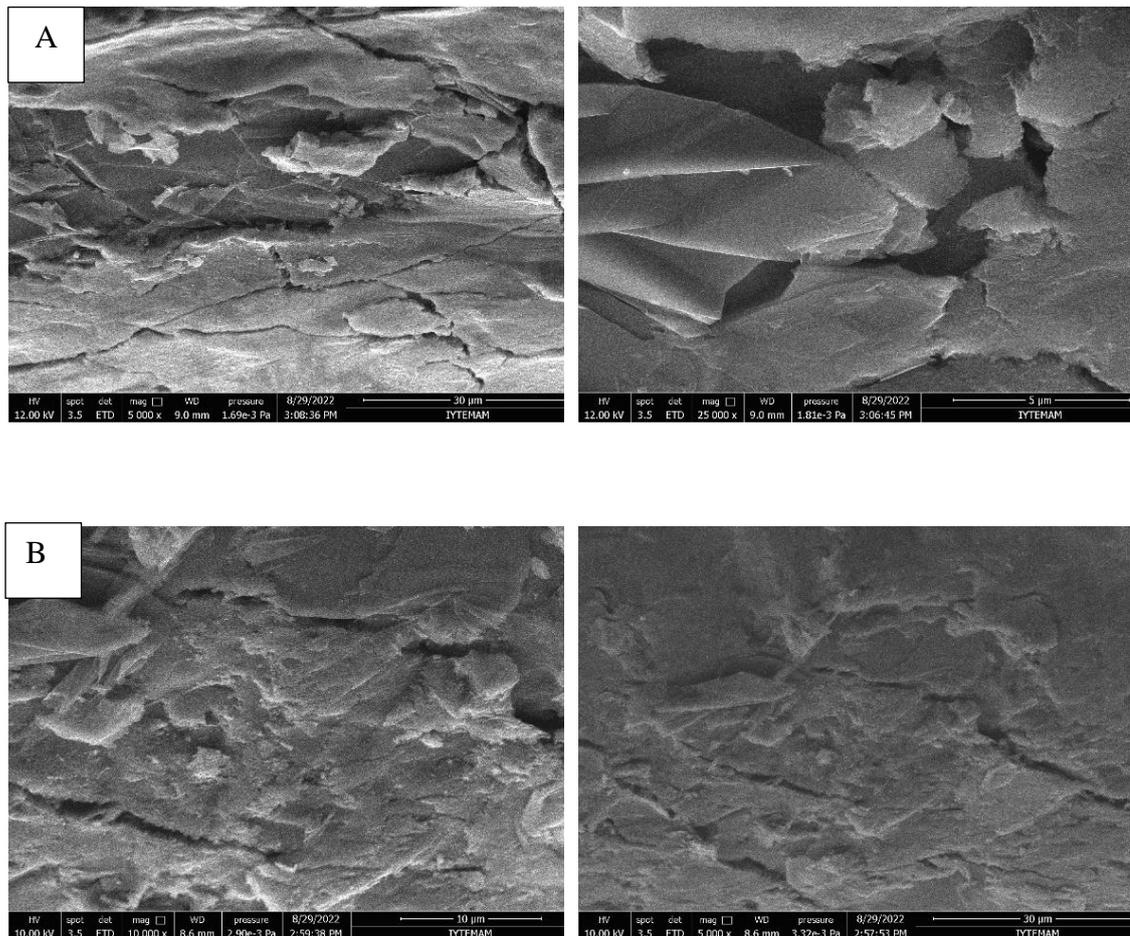


Figure 24. Characterization of conductive inks. (A) SEM image of ink with graphene exfoliated with ethylene glycol and carbon black (B) SEM image of ink with graphene exfoliated with DMF and carbon black (C) SEM image of ink with graphene exfoliated with NMP and carbon black.

(cont. on next page)

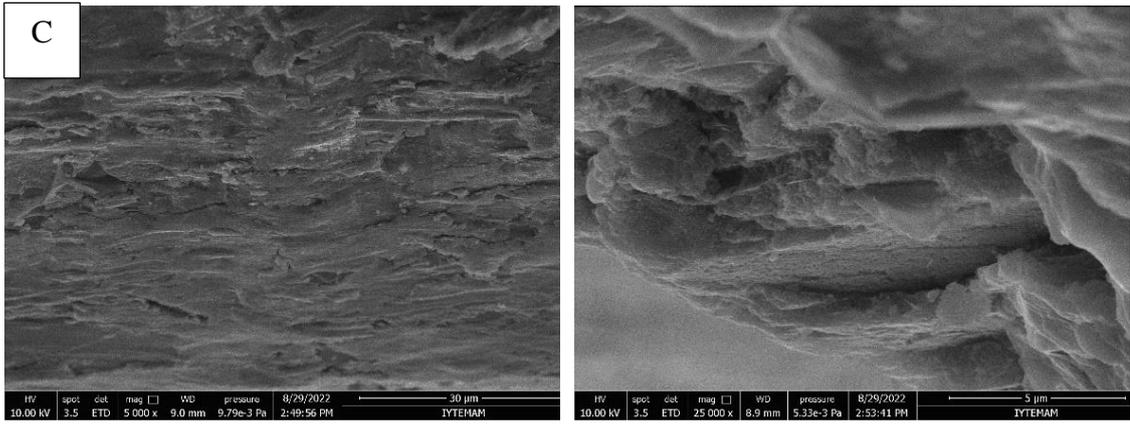


Figure 24. (cont.)

CHAPTER 7

CONCLUSIONS

Graphite/Carbon black based conductive ink by using ball milling method is produced. The aim of this study was to investigate exfoliation liquid and graphite to carbon black ratio effect on conductivity, particle size and rheology of printed surfaces.

Exfoliation liquid, which was NMP, DMF, ethylene glycol and water, effect were investigated on electrical properties by using ball milling. Minimum resistivity 0.02 k Ω was obtained when using NMP. Also, this sample had lowest particle size distribution than other samples. When average particle sizes compared the sample with NMP was exfoliated better than the others.

Graphite to carbon black effect on the conductivity of printed ink was investigated with 0.5, 0.75, 1, 1.5 and 2 ratios. Graphite to carbon black ratio of 1 containing had the highest electrical properties with 0.045 k Ω . An increase in graphite content from 0.5 to 1 gave an increase in conductivity. Increases in graphite content beyond the optimum loading resulted in higher resistance. The reason of this situation, graphite particles were close together and coated in a varnish/carbon black matrix which also acted as conductive filler bridging between neighboring graphite particles., at high graphite ratio. At low graphite content, the graphite particles tend to be isolated from one another, with the varnish/carbon black matrix forming the bulk of the ink and heavily coating most of the graphite particles.

Rheological properties of conductive inks are critical for determination of processing methods of conductive inks. Exfoliation liquid effect on viscosity and thixotropy was investigated. All samples exfoliated with different liquids showed shear thinning behavior. Dispersion exfoliated with NMP had higher viscosity than other inks. The reason behind that situation is related with effected exfoliation and size reduction of graphite. Highest thixotropy was recorded as 1801 Pa.s⁻¹ for ink exfoliated with water . This value was at least 10 times higher than other conductive inks and had the lowest conductivity.

G/C ratio effect, at ratios of 0.5, 0.75, 1, 1.5 and 2, on viscosity and thixotropy of conductive was investigated. All samples behaved shear thinning and highest viscosity

was measured at ink with 0.5 G/CB content. Thixotropic behavior of that ink was also higher than others. The situation is related with high concentration of fine carbon black particles and this sample also had the lowest conductivity. Increase of thixotropy over $1000 \text{ Pa}\cdot\text{s}^{-1}$ resulted in higher resistances for inks prepared with different exfoliation liquid and G/CB ratios.

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