Study of the Optimization of Hansen Solubility Parameters in the Ultrasonic Exfoliation Technique to Achieve Stable Graphene Dispersions

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Abstract

Graphene synthesis by ultrasonic exfoliation of graphite in organic solvents yields good concentrations of graphene dispersions. This technique is extremely versatile, economical and environmentally friendly. The technique depends on the matching of the surface energy of graphite and solvent which can also be expressed through Hansen solubility parameters (HSP). HSP refers the three parameters, δD for dispersion (van der Waals), δP for polarity (related to dipole moment) and δH for hydrogen bonding. The matching of surface energy is related to minimizing the HSP deviation, R_a. The R_a can be modified by mixing two solvents. According to HSP theory, a decrease in R_a leads to an increase in solubility. Hence maximum solubility should be achieved at minimum R_a. In this study, exfoliation of graphite was performed using a binary solution of low boiling point solvent i.e., isopropyl alcohol (IPA) and water. The theoretical calculations were performed using HSP theory with variation of IPA content in deionized water 0% to 100% v/v with 20% increments. In the experimental part, dispersions were characterized for turbidity and stability. The quantification of dispersions was done by UV-Vis spectroscopy. The experimental results were found to be consistent with the theoretical studies and maximum dispersion was obtained at the minimum value of R_a. The study confirms that the tailoring HSP technique could give better dispersions in binary solutions with optimized mixing ratios and could be used for the scalable production of graphene using numerous binary solvent mixtures.

Keywords: Graphene, Hansen solubility parameters, dispersions, isopropyl alcohol.

Introduction

Graphene is a 2-dimensional sp2-bonded structure of carbon-based material existing as a single layer carbon atom arranged in honeycomb lattice (Razaq et. Al,2022). Its attractive properties such as the

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highest known strength with a Young's modulus of TPa, high thermal conductivity of ~ 5 x 10^3 $Wm^{-1}K^{-1}$ and excellent electrical mobilities of over 200,000 $cm^2V^{-1}S^{-1}$ at electron densities of ~ 2 x 10^{11} cm^{-2} have stimulated much research since its discovery (Lee et.al., 2021)(Ullah et.al,2021). There are various applications of graphene-based materials such as nanoelectric devices (Emiru et.al., 2017), gas sensors (Varghese et.al., 2015), storage devices (Lv et.al., 2017) (Olabi et.al.,2021), optical electronics (Pardhan et.al., 2017), and water desalination (Han et.al., 2021).

Among various methods, ultrasonic exfoliation of graphite in certain solvents produces facile, green, scalable and low-cost graphene dispersions (Zhong et.al., 2015) (Amiri et.al., 2018). This method requires matching the surface energy between the solute and solvent. Solvents with surface energies in the range of ~ 40-50 mJm^{-2} are considered to be good solvents (Johnson et.al.,2015) (Gomez et.al.,2021). Currently, solvents that fulfil this requirement have a high boiling point (~ 200 ºC) and are expensive. Studies have shown that high boiling point of these solvents makes it difficult to be completely removed from the system and the residual solvent can be detrimental for composites (Çelik et.al. 2017). Therefore, it is necessary to explore the possibility of low boiling point solvents to reduce cost and simplify the process of graphene synthesis. An alternative approach to characterize solvents is the Hansen solubility parameters (HSP) technique. This technique can show that two bad solvents can predictably combine to form a good solvent.

In this study, the HSP theory was used on two mediocre low boiling solvents, water (100ºC at 760mm of Hg) and isopropanol (IPA) (82.5ºC at 760mm of Hg) to produce a good solvent whose solubility parameters match the HSP parameters of the solute. It was found that different ratios of IPA and water produce binary solvent, close to HSP parameters, compatible with graphite. The produced dispersions were characterized for turbidity and quantification through UV-Vis spectroscopy. An optimized dispersion of graphene was obtained when the water/IPA mixing ratio was 40/60.

Materials and methods

Chemicals

Graphite powder (mesh size < 230) and isopropanol (IPA) (Duksan reagents, Korea) were purchased from the local supplier.

Sample preparation

Two samples labeled 1 and 2 were made by dissolving 90 mg of graphite powder in 30 ml deionized water and in 30 ml IPA, respectively.

The other samples have 60/40, 40/60 and 20/80 v/v mixing ratios of deionized water to IPA mixtures, (Table 1).

All samples were sonicated for 2 hours in an ultrasonic bath. The water bath was continuously refilled to control the temperature of the water during the experiment. The samples were then centrifuged at 1000 rpm for 30 minutes. The supernatant was removed by dropper and left for 1 week under ambient conditions to check the stability of the dispersions.

Table 1
Composition of pure and mixed solvent samples

Sr. no.	Sample Name	Solvent
1	Sample 1	DI water 100%, IPA 0%
2	Sample 2	DI water 0%, IPA 100%
3	Sample 3	DI water 60%, IPA 40%
4	Sample 4	DI water 40%, IPA 60%
5	Sample 5	DI water 20%, IPA 80%

Characterization

The quantification of turbidity of samples for comparison purposes was investigated using UV-Visible spectrophotometer in wavelengths ranging from 400 nm to 800 nm in spectrum mode.

Analytical method

The Hansen solubility parameters (HSP) technique is used to predict the maximum graphene dispersion in different water/IPAbinary solvent. It uses three parameters δD for dispersion (van der Waals), δP for polarity (related to dipole moment) and δH for hydrogen bonding. Deviation of the solubility parameter between solvent and solute is represented by R_a.

$$R_a = (4(\delta_{D1}-\delta_{D2})^2+(\delta_{P1}-\delta_{P2})^2+(\delta_{H1}-\delta_{H2})^2)^{1/2}.$$

According to HSP theory, a decrease in Ra leads to an increase in solubility. Hence the maximum solubility should be at the minimum value of R_a (Zhu et. Al.,2021).

Results and Discussion

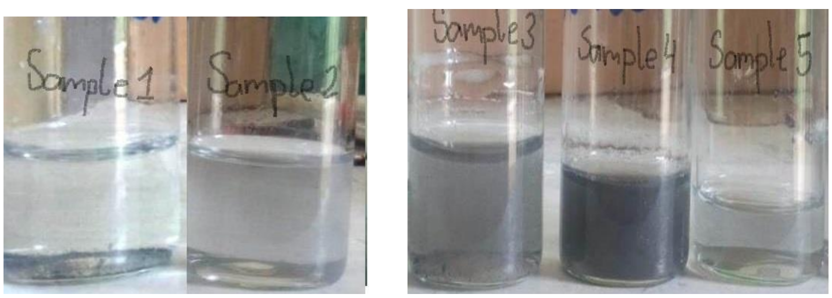
Theoretical calculations using HSP theory

HSP theory was used for theoretical calculations of graphene dispersions in pure solvents and solvent mixtures. The solubility parameters of each solvent were plotted as coordinates in 3D Hansen space. These parameters are tabulated in Table 2.

Table 2
HSP parameter and deviations of pure and mixed solvent samples

Sr. no.	Sample Name	δD	δP	δH	R_a
1	Sample 1	18.1	17.1	16.9	12.063
2	Sample 2	15.8	6.1	16.4	10.261
3	Sample 3	17.18	12.7	16.7	9.759
4	Sample 4	16.72	10.5	16.6	9.338
5	Sample 5	16.26	8.30	16.5	9.516

When mixture of pure solvent and graphite was subjected to sonication, highly turbid and black dispersions were obtained. These dispersions were extremely unstable and when stored under ambient conditions, precipitation of graphite powder occurred. It is evident from Figure 1a that samples containing pure deionized water and IPA show minimum turbidity after a week which indicates minimum graphene production.



(a) (b)

Figure 1. Graphene dispersions in: a) pure deionized water and IPA, b) water/IPA mixtures

In the case of IPA/water mixtures, the turbidity of the samples was retained when stored under ambient conditions. The maximum turbidity is observed in the 40/60% DI/IPA mixture, which is in accordance with the theoretical calculations of the HSP distance. The trend in Ra shown in Table 2 was found to depend upon the volume proportions of constituent solvents. The maximum dispersions were obtained at the optimum volume fraction, and were clearly observed by the turbidity of each sample.

UV-VIS spectroscopy was performed with a Shimadzu UV-1800 in wavelength range from 200 nm to 800 nm. The absorbance versus wavelength relation for the 0% IPA volume fraction and for the 100% IPA volume fraction can be visualized in Figure 2.

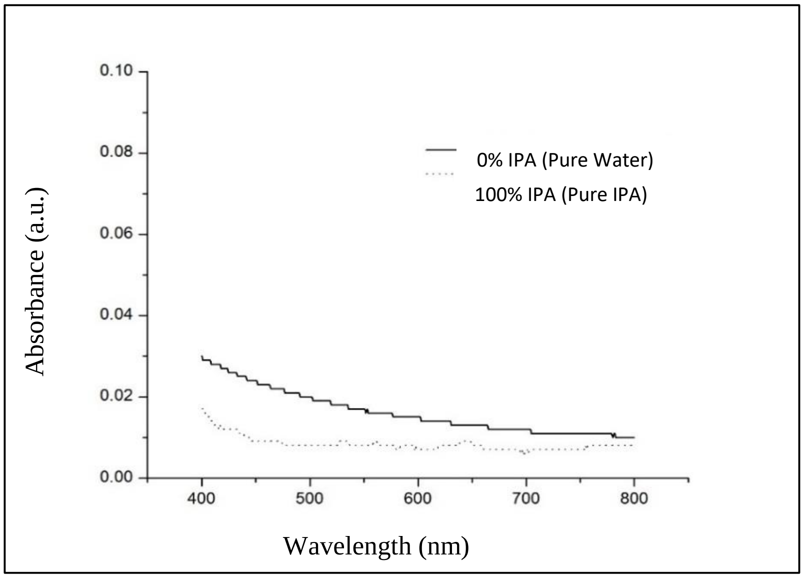


Figure 3. Absorption spectra for sample 1 (0% IPA volume fraction) and sample 2 (100% IPA volume fraction)

The absorbance was found to be very low for sample 1 (pure water) and for sample 2 (pure IPA) (Figure 3).

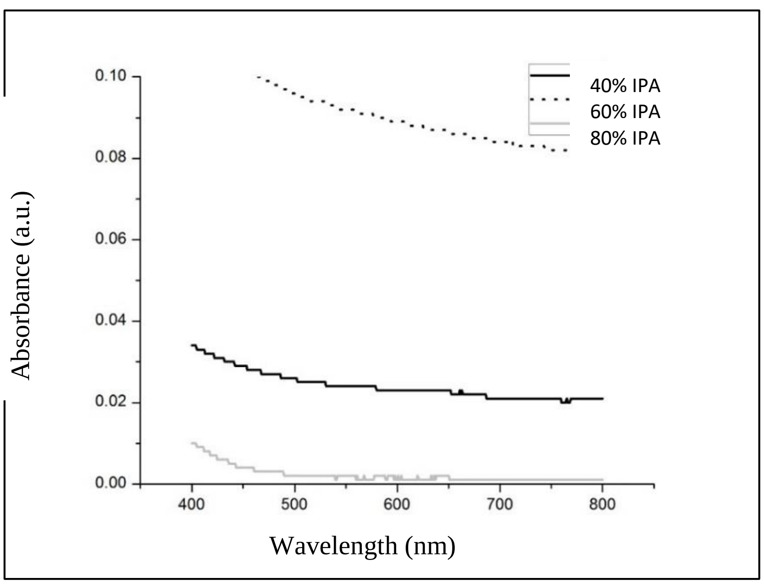


Figure 4. Absorption spectra for the other samples.

The UV-VIS spectra for samples 3, 4 and 5 show that the maximum absorbance was attained in sample 4 which contained the maximum graphene dispersion (Figure 4). Hence the composition of sample 4 was considered the most suitable one. This result further confirms that specific mixing ratios of solvents could give high graphene concentrations, as shown by high graphene dispersion. Hence the experimental results are obtained in accordance with the theoretical results.

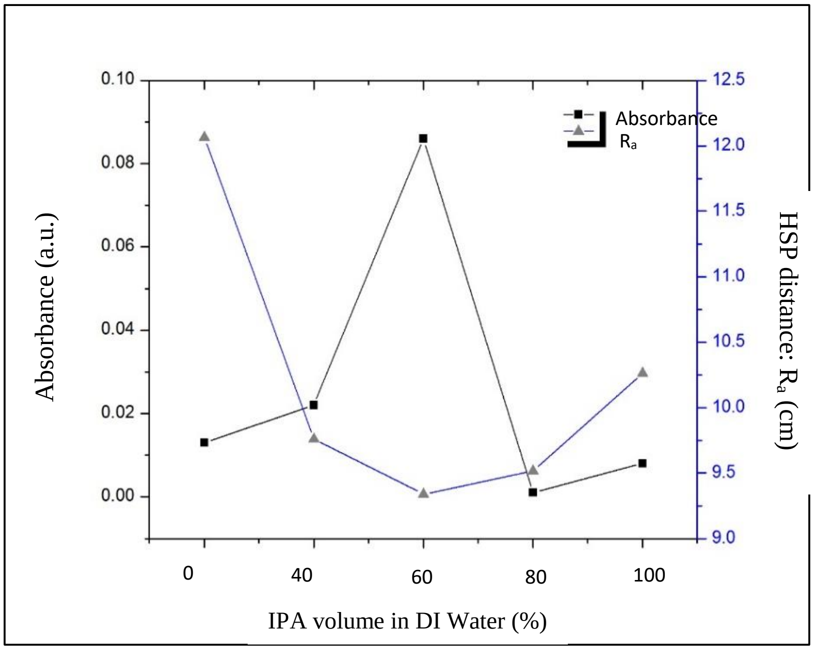


Figure 5. Relation between Ra and absorbance at various IPA volume fractions.

Figure 5 shows the relation of solvent samples with HSP deviation and absorbance. It is clearly observed that samples with larger deviations Ra, have minimum absorbance indicating the minimum turbidity. On the other hand, the sample with the minimum Ra possesses the largest absorbance indicating the maximum graphene production.

Conclusion

One of the problems with ultrasonic exfoliation method of graphene production is that the best solvents are expensive and tend to have high boiling points and so are difficult to remove and can present problems for flake deposition and composite formation. In this study pure high boling solvents were successfully replaced by mixtures of low boiling point and inexpensive solvents with changing proportions of (v/v %) mixing. The study has successfully used Hansen solubility parameters and achieved the highest graphene concentration at minimum deviation R_a.

These dispersions were reasonably stable after 100 hours. This approach of tailoring HSP, can be easily applied to various solvent systems and its scope could be extended for large-scale production of graphene in low-boiling-point solutions such as water/IPA mixture.

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