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Effect of Alcoholic Molecules (2-Propanol) Blending on Exfoliation of Graphite Flakes

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Abstract: ***In present research, alcoholic molecules (2-Propanol) were blended with Intercalated Graphite to improve expandability of Intercalated Graphite Flakes. Very small amount of 2-Propanol rapidly increases expandable volume. Exfoliation characteristics were also improved. Various analysis were carried out to determine total volume expansion, microstructure and planer deformation. Results were compared with that of some conventional methods. Results show that blending of 2-Propanol with acid intercalated compound gives volume expansion up to 2-3 times higher than that of conventional methods. XRD analysis shows that characteristic peak of graphite at $2\theta = 26^{o}$ referring 002 reflections was found weakened in Exfoliated flakes with 2-Propanol blending. This shows disruption of planer structure and conforms high degree of planer deformation indicating high degree of exfoliation in 2-Propanol blending method as compared to other methods. SEM micrographs are also evidencing good exfoliation. Proposed theory behind above mentioned results is that, alcoholic molecules like 2-Propanol reacts with acidic functionality present on the intercalated flakes and gets attached on planer edges. On the edge of graphitic plane, these molecules act as obstacle to diffusing gases resulting in increased pressure of decomposition gases. These more pressurized gases move planes more apart to each other resulting in high volume expansion.***

Keywords: Exfoliation, Intercalation, 2-Propanol, Expandable Graphite, Graphite Flakes.

1. Introduction

Intercalation and Exfoliation of Graphite is major concern of researchers from various streams from last few decades. Intercalated Graphite is the compound obtained after insertion of various atoms or molecules inside spacing of the planer stacking of Graphite. Exfoliation of intercalated Graphite involves rapid decomposition of intercalated moieties resulting in increase of inter planer spacing of Graphite [1]. These expands graphite several hundred times along the c-direction.

Exfoliated Graphite is puffed-up material with very low density, high thermal insulation and thermal stability [1], [2]. It has enormous application in high tech materials and processing [3]. Compression of Exfoliated Graphite results in good lubricating material and flexible graphite sheet [4]. It found major application in high temperature sealing and lubrication. Exfoliated Graphite is also promising candidate as a filler in matrices like Polymers and paints etc. [5]–[7]. It is also promising material as absorbent in oil industries [8], [9]. There are various conventional methods to produce Exfoliated Graphite [1], [10], [11]. Acid intercalation is the most convenient and popular method amongst industries [1], [10], [11]. Herein, present research shows compar2n of various methods of acid intercalation over expandability and exfoliation characteristics. Along with that, some modifications were done in conventional methods to improve final product. Graphite samples were intercalated by mixture of Conc. HNO_3 and Conc. H_2SO_4 as conventional methods [11]. Where as in modified method, intercalated compound was blended with 2-Propanol in various concentration. Various analysis like Bulk Volume, SEM and XRD were carried out to conform the theory.

2. Experimental

Two samples of Natural Graphite Flakes were used for this study. First type of flakes namely FL1 was with particle size between 600-700 µ and the other type namely FL2 was with particle size between 150-250 µ. All chemicals used in present experiments were analytical grade.

2.1 Intercalation

Both Graphite flake samples were intercalated by H_2SO_4 + HNO_3 mixture with 7:3 ratio respectively. To avoid washing and drying steps, flakes were blended with little excess of the sufficient amount of acid mixture to produce 1-stage intercalation. The intercalation procedure was followed as below. 5 g Graphite flakes were mixed with 20 ml mixture of H_2SO_4 + HNO_3 in 7:3 ratio respectively. It was gently mixed in 100 ml beaker for 10 minutes. This mixture was kept in 120 ^{o}C oven for 1 hour.

2.2 2-Propanol Blending

As mentioned in above section 2.1, another set of graphite flakes mixed with acid mixture was prepared. 5 g of Graphite flakes were mixed with 20 ml acid mixture prepared as mentioned above in section 2.1. It was gently mixed in 100 ml beaker for 10 minutes. 1 g 2-Propanol was added and again mixed for 10 minutes. This mixture was kept in 120 ^{o}C oven for 1 hour.

2.3 Exfoliation

Samples obtained from intercalation with and without 2-Propanol blending were subjected to exfoliation. These samples were exfoliated in container preheated at 600 ^{o}C and

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1000°C. Exfoliation was carried out in two ways. One portion of sample was exfoliated by pouring 1 g sample into the container preheated at approx. 600 °C and the other portion of 1 g poured into the container preheated at 1000 °C. Poured samples were given 1 minute exfoliation time to ensure complete exfoliation and then removed from heating.

Final samples were abbreviated as mentioned below,

FL1_WB_600 : Flakes FL1 / intercalated / without 2-Propanol blending / exfoliated at 600 °C
FL1_WB_1000 : Flakes FL1 / intercalated / without 2-Propanol blending / exfoliated at 1000 °C
FL1_IPA_600 : Flakes FL1 / intercalated / with 2-Propanol blending / exfoliated at 600 °C
FL1_IPA_1000 : Flakes FL1 / intercalated / with 2-Propanol blending / exfoliated at 1000 °C
FL2_WB_600 : Flakes FL2 / intercalated / without 2-Propanol blending / exfoliated at 600 °C
FL2_WB_1000 : Flakes FL2 / intercalated / without 2-Propanol blending / exfoliated at 1000 °C
FL2_IPA_600 : Flakes FL2 / intercalated / with 2-Propanol blending / exfoliated at 600 °C
FL2_IPA_1000 : Flakes FL2 / intercalated / with 2-Propanol blending / exfoliated at 1000 °C

3. Results and Discussion

It is well known that in intercalation process acid molecules get inserted in between inter planer spacing of raw graphite particles. During exfoliation these foreign molecules get sudden decompose at high temperature. These decomposition gases generate pressure in between two basal planes moving them apart to each other. Therefore Exfoliation is a process in which graphite expands tremendously in c – direction. This leads to production of puffed up material having vermicular type particles. Expansion of the graphite particles depend upon pressure produced during high temperature treatment. There are other parameters which play crucial role in production of pressure between two planes. These parameters are (i) type of intercalated moiety, (ii) rate of temperature increase or rather exfoliation temperature and (iii) particle size etc.

In present research, same type of intercalate molecules were used throughout all experiments. 2-Propanol was blended with intercalated compound to increase pressure of decomposition gases. Role of 2-Propanol during entire process is shown in Fig. 1. Proposed theory of this effect is as below.

After intercalation of acid molecules Graphite flakes contain acidic functionality at the edge of graphitic planes. 2-Propanol is a molecule having alcoholic –OH group at middle carbon. As shown in Fig.1, this alcoholic –OH reacts with acidic functionality of intercalated compound and produces hindrances at the edge of graphitic planes. During exfoliation this molecules resist decomposition gases to diffuse out at the ends of planes. A diffusion gas gets sufficient time to produce more pressure in between two basal planes resulting in more separation of planer structure. While in other context, diffusion gases pass out easily from the inter planer spacing.

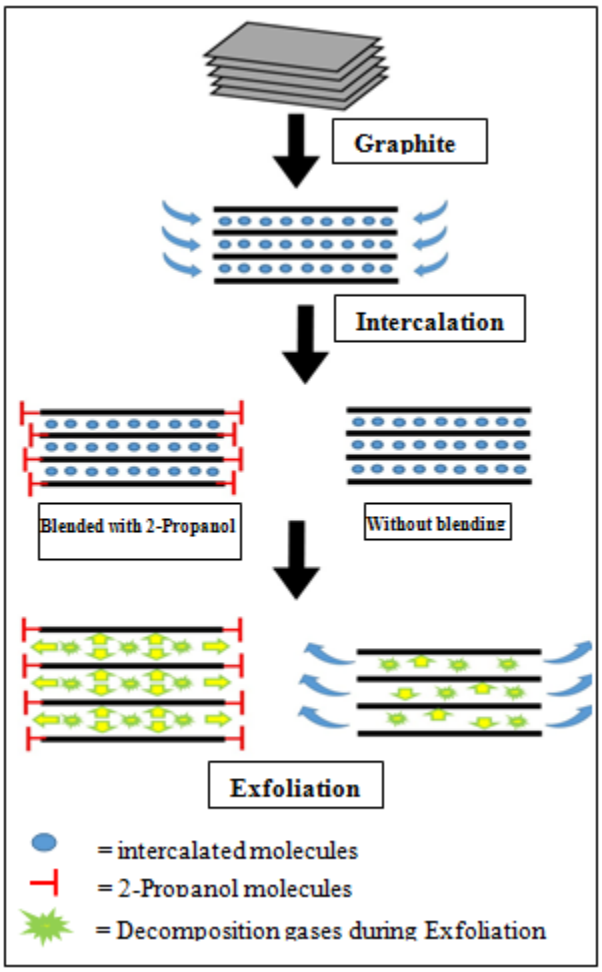


Figure 1: Schematic diagram of intercalation and exfoliation process of Graphite flakes with and without 2-Propanol blending.

To confirm these assumptions, exfoliated graphite samples were analyzed by various methods as mentioned below,

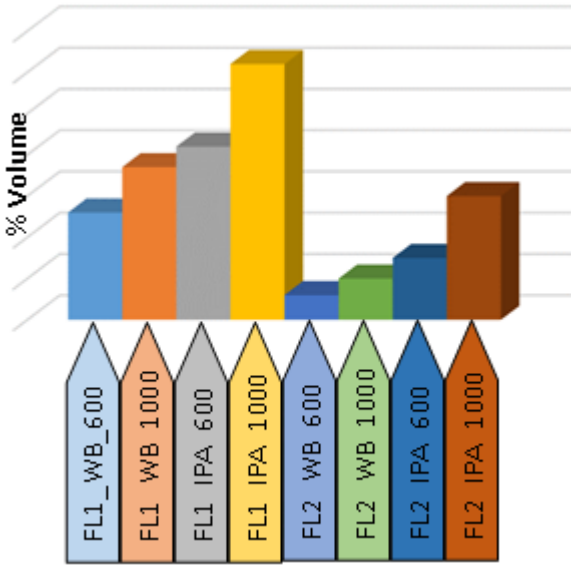


Figure 2: percentage volume of Exfoliated samples with compared to volume of raw Graphite flakes.

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3.1 Average Volume Expansion

Average volume expansion was determined by careful funneling of raw graphite flakes, intercalated graphite flakes and exfoliated graphite flakes into the volumetric flask. Fig.2 shows compar2n between percentage volume expansions of various exfoliated flakes. Results shows that percentage of volume expansion increases tremendously with 2-Propanol blending. Irrespective to the flake size and exfoliation temperature 2-Propanol blending gives better expansion.

3.2 XRD

To determine degree of Exfoliation XRD analysis were carried out by standard powder XRD method by direct pouring sample in to sample holder without external pressing. Cu target tube was used and scan steps were kept 0.007° interval.

Fig.3 shows characteristic peak of Graphite at $2\theta \approx 26^{o}$ and corresponding peak of same reflection in Exfoliated flakes with and without 2-Propanol blending. Sharp and very high peak of raw graphite flakes FL1 shows that it is having very good planar stacking. While exfoliated product of 2-Propanol blended flakes shows more weakened peak than flakes without blending. Weakening of characteristic peak indicates disruption of planer stacking and hence more separation of the planes. XRD results are in good conviction with other results.

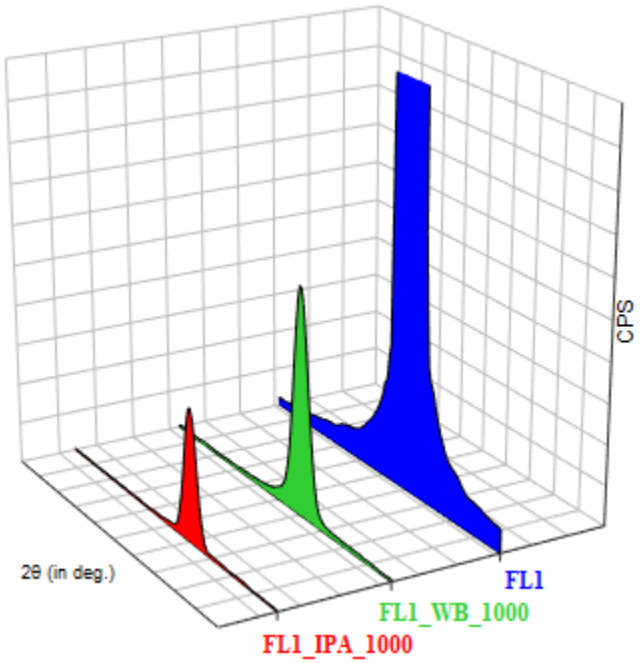


Figure 3: XRD Graph of Raw Flakes (FL1); Exfoliated Flakes without 2-Propanol blending (FL1_WB_1000) and with 2-Propanol blending (FL1_IPA_1000)

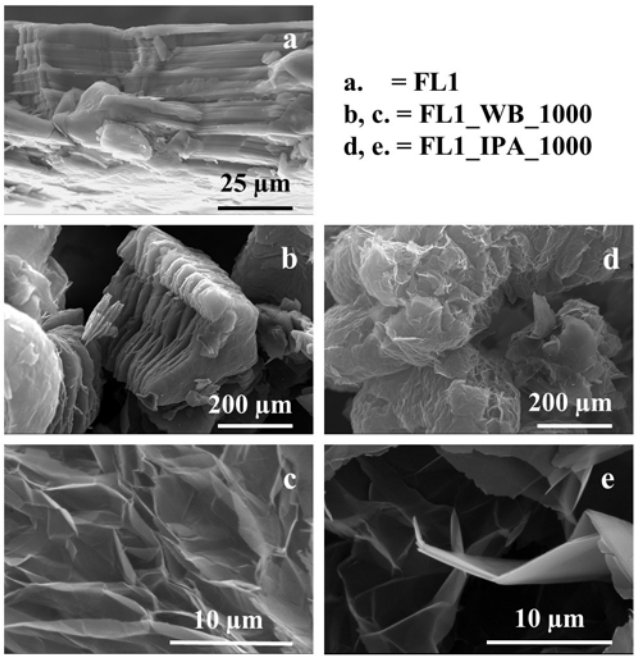


Figure 4: SEM illustrations of Raw Flakes and Exfoliated Flakes with and without blending at various Magnifications.

3.3 SEM

Fig.4 shows SEM micrographs of Raw Flakes FL1 and Exfoliated Flakes with and without 2-Propanol blending for compar2n. Fig.4a is micrograph of Raw Graphite Flake FL1. It is very difficult to distinguish planer stacking because of very compact packing of planes in Raw Graphite Flakes. While in Exfoliated samples micrographs from Fig.4b to e shows separated platelets. Fig.4b and d both are micrographs of Exfoliated Flakes without and with 2-Propanol blending respectively at same magnification. Fig.4b shows opened up pores between graphitic platelets but still stacking is not clearly disturbed while in Fig.4d Exfoliated Flakes with 2-Propanol blending shows totally puffed up morphology of planer stacking. It clearly illustrates high degree of Exfoliation in 2-Propanol blended sample with respect to Exfoliated Flakes without 2-Propanol blending.

In addition to this, Fig.4c and e show micrographs of the Exfoliated Flakes without and with 2-Propanol blending respectively at high magnification. Micrograph of Flakes without blending in Fig.4c shows comparatively poor exfoliation causing platelets of multi Graphitic planes. While it shows separation of Graphitic planes from single to few layer in 2-Propanol blended flakes. SEM illustrations are in good accordance with results of volume expansion and XRD analysis.

4. Conclusion

In present research, major concern was to increase exfoliation volume by resisting or say hindering Decomposition Gases from diffusing out during exfoliation. Slow diffusion of gases causes high pressure between two layers of Graphite. This causes high degree of Exfoliation. Herein, 2-Propanol molecules were utilized for such purpose. Alcoholic Hydroxyl group of these molecules reacts with

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acidic functionalities of Intercalated Graphite Flakes. Other branches of this molecule creates obstacle at free openings of planer stacking. Hence, upon exfoliation at fraction of moment it hinders decomposition gases from diffusing out. As a result 2-Propanol blended Intercalation compound expands more than conventional intercalation compound.

Results from various analysis have good consistency with above mentioned theory. Determination of total volume expansion shows 2-3 times more volume expansion of 2-Propanol blended flakes than conventional one. This behavior is consistent irrespective to Raw Flake size and Exfoliation Temperature. While XRD analysis also indicates more planer disruption of 2-Propanol blended compound. In accordance to these, SEM shows highly puffed up morphology of 2-Propanol blended sample than without blended one.

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