

Mechanically Stable Nano-graphite Polyaniline Composites: Synthesis and Characterization

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ABSTRACT: Flexible electronics materials demand better mechanical properties along with electronic conductivity. However, these materials in their pure form are relatively more susceptible to structural failures, limiting flexibility for electronic applications, which is impeding its growth in commercial use. Therefore it is necessary to improve their respective properties by means of additives, fillers etc. Graphite powder has been an effective filler material to enhance the mechanical and electrical properties which can be further improved by using graphite in its nano-form. We report effect of reinforcement of nano graphite powder on hardness and electrical conductivity of PANi. The nano graphite powder is prepared by planetary ball milling with different time cycles and characterized by scanning electron microscope, transmission electron microscope. Polyaniline (PANi) and its composite are prepared in the form of pellets. The pellets are prepared by cold pressing. The graphite filled PANi composites are characterized for electrical conductivity and hardness. The outcome of this work is the composite materials with improved mechanical and electronic performance.

KEYWORDS: Nano Graphite, Ball Milling, Pani / Its Composites, Mechanical Properties.

I. INTRODUCTION

Carbon, the 6th element in the periodic table, is truly remarkable for its extraordinary ability to combine with itself and other chemical elements in different ways. In nature, it is abundantly available in the form of coal and graphite. The graphite crystal consists of stacks of parallel, two dimensional, graphene sheets (a single carbon layer in the crystalline honeycomb graphite lattice is known as a graphene layer or graphene sheet) with sp² hybridized carbon atoms tightly bonded in the hexagonal rings [1]. Graphite is anisotropic due to the difference between in-plane and out-of-plane bonding of the carbon atoms. The p^z orbital is distributed over the entire graphene sheet making it thermally and electrically conducting [2]. The layered structure of graphite exhibits three dimensional orders and is shown in Fig 1.

It is evident that materials show higher activity at lower scales such as nanostructures [2]. There are broadly two methods, chemical and physical, are employed to obtain the nanostructures. The physical routes considers top down approach i.e. bulk material is disintegrated in smaller particles. . In case of graphite, high surface area nano graphite can be produced via micro mechanical exfoliation. However, the yield of this process is very low [3]. Graphite in nano form possess excellent mechanical, thermal, electrical properties, high surface area and excellent dimensional stability leading to wide applications such as transistor, battery, super capacitor, fuel cell, biosensor, composites and so on.

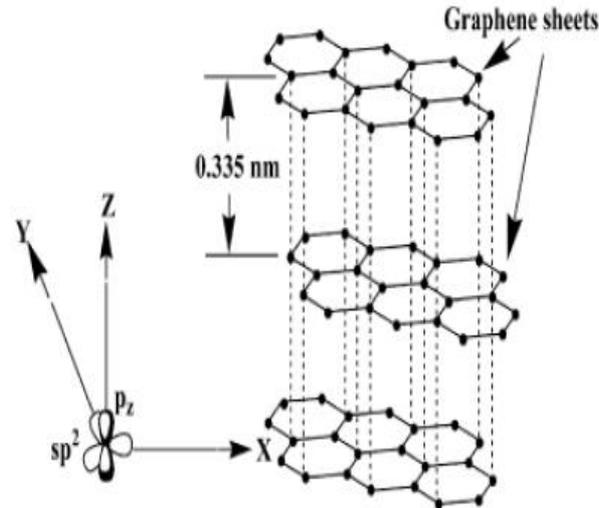


Figure 1: Layered structure of graphite showing the sp^2 hybridized carbon atoms tightly bonded in hexagonal rings [2].

Mechanical milling has been known to be an effective way to prepare nano crystalline structures and thus used to produce high surface area nano graphite powder. A ball mill is a type of grinder used to grind materials into extremely fine powder. Various materials are used as media, including ceramic balls, flint pebbles and stainless steel balls. An internal cascading effect reduces the material to a fine powder. Large to medium-sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion). High quality ball mills are potentially expensive and can grind mixture particles to as small as 5 nm, enormously increasing surface area and reaction rates [4].

This paper is organized as follows. Section 2, presents the detailed methodology of preparation of nano-graphite powder, PANi and composites. In section 3, we present the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) of the ball milled graphite powders, followed by the results of effects of reinforcement, of high surface area graphite, on the hardness and electrical conductivity of PANi + Nanographite composites [5].

II. EXPERIMENTAL WORKS

2.1 Ball milling of Graphite

Natural graphite was powdered by mechanical milling in planetary ball mill equipped with tungsten viol containing stainless steel balls (7.8 g/cm^3) and zirconia balls (5.68 g/cm^3). The milling of graphite was carried out for 100 min, 200 min and 300 min [6, 7].

2.2 Synthesis of PANI

Polyacrylic acid (PAA) (0.001-0.1M) powder was used as the template and was stirred with 100ml double distilled water until; the powder is dissolved [8]. Then (0.1M) aniline monomer was added in polyacrylic acid solution and stirred for 24 hr at room temperature. Solution was acidified with Sulfuric acid ($\text{H}_2\text{SO}_4 - 0.5\text{M}$) and 0.1 M Ammonium Persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was added drop by drop after the interval 1hr. During this process pH was maintained at 4. At this stage the product becomes dark green. Solution was pre-cooled for 12 hrs. up to $1-5^\circ\text{C}$. The precipitated emeraldite salt is filtered and washed repeatedly with distilled water until the filtrate becomes colourless and dried at 40°C in oven [9].

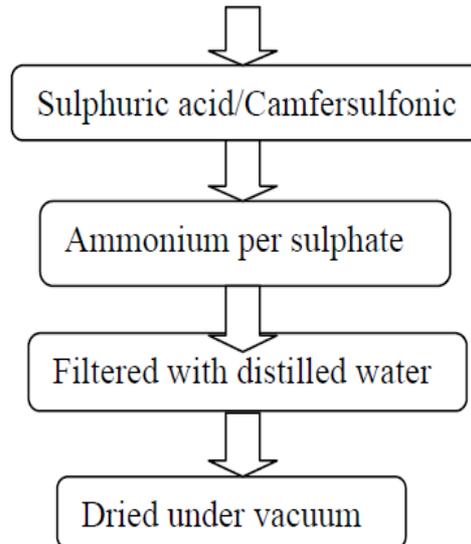


Figure 2: Process flow for synthesis of Polyaniline

2.3 Preparation of composites

Composite of polyaniline and high surface area graphite powder was prepared by mixing polyaniline with varying weight percentage of graphite powder. Pellets of 500 milligram are prepared and accordingly fractions of PANI and graphite were mixed. First polyaniline was powdered by using mortar pestle, manually. Then graphite powder was added to it. This mixture was ball milled for 20 minute for uniform mixing of powders and then taken for compaction under hydraulic press. Pellets of 15 mm diameter were then compacted at the load of 5 ton using hydraulic press. The proportion of graphite nano powders [milled for 100 min, 200 min and 300 min] in PANi is varied from 10 % to 60 % with the increment of 10%.

III. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM):-

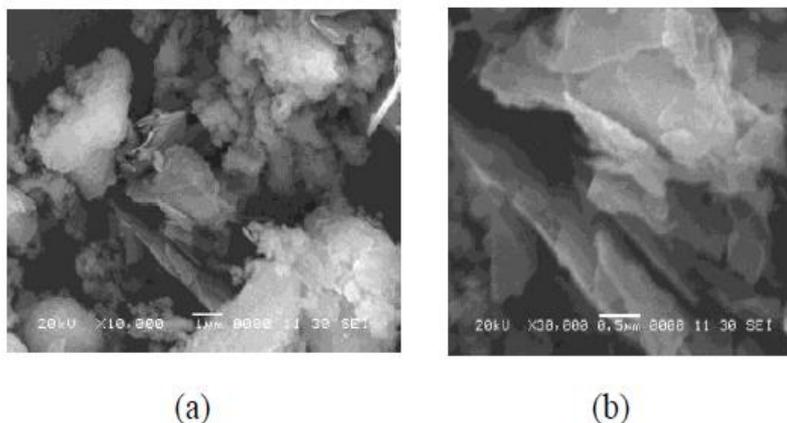


Fig 3 SEM image of graphite after 100 min milling with SS balls

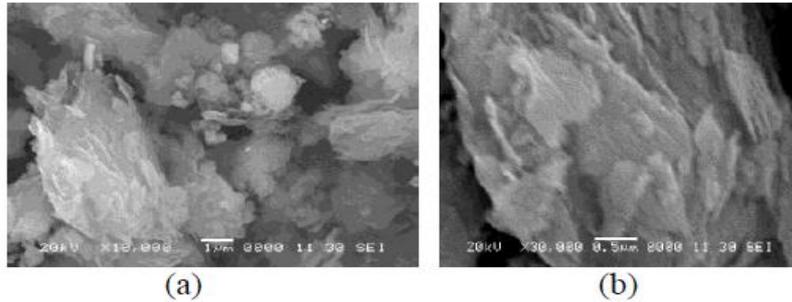


Fig 4 SEM image of graphite after 200 min milling with SS balls

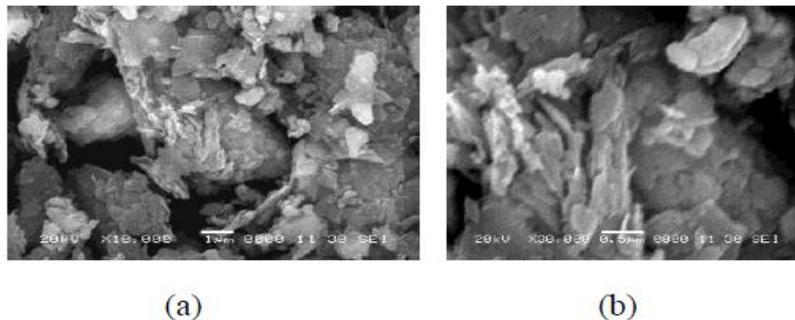


Fig 5 SEM image of graphite after 300 min milling with SS balls

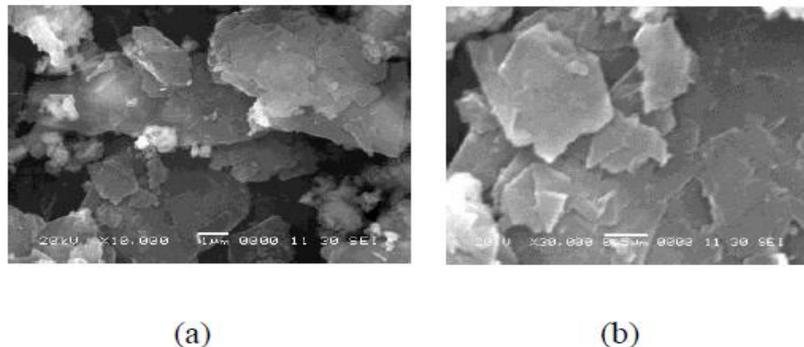


Fig 6 SEM image of graphite after 100 min milling with Zr balls

SEM images of milled graphite powder samples were obtained for different magnification. Figures 3 to 5 shows the morphological changes in the process of mechanical milling, of graphite with SS balls, with increasing milling time. Figures 3 to 6 clearly depicts the formation of graphite nano sheets. But as milling time increased from 100 min to 200 min, the smaller particles of graphite are seen to be piled over bigger particles due to higher surface energy of these particles and aggregate structures are formed as seen in fig 3 and 4. Therefore it is concluded that the particle agglomeration increases as milling time is increased. Figure 6 shows morphology of 100 min ball milled graphite with Zr balls, having same diameter as of SS balls. However the sheets formed are larger in size than that of using SS balls. It can be understood that the higher the density of balls used for milling causes higher impact energy which lead to smaller particle (sheet) size. The Transmission Electron Microscopy was performed to confirm whether the single layer graphene is obtained and to obtain more detailed structural details.

3.2 Transmission Electron Microscope (TEM)

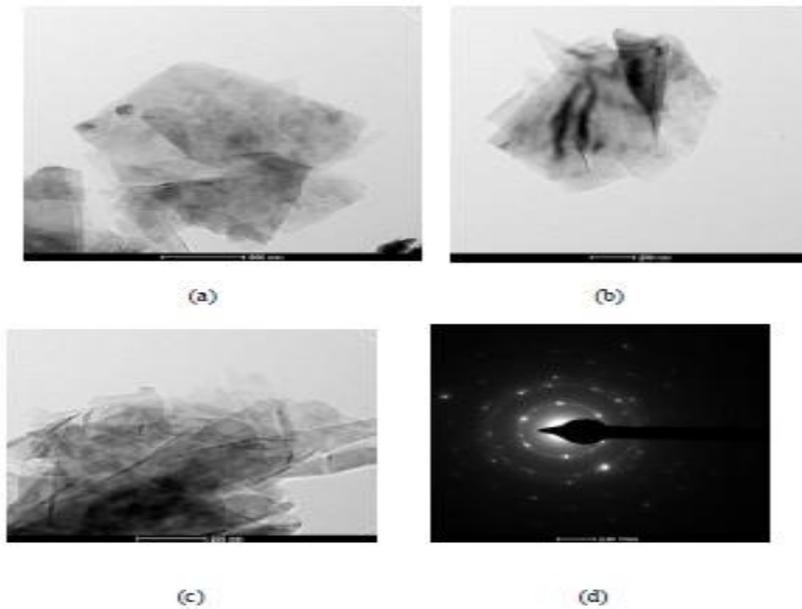


Fig 7 a, b, c shows TEM image of graphite after 100 min milling with SS balls
d) Diffraction image of graphite after 100 min milling with SS balls

Graphite powder produced by SS balls showed a fractured and deformed morphology due to higher energy input resulting in breakage of the carbon-carbon covalent bonds by the denser SS balls. Figure 7 (a, b, c) shows the layer by layer structure of graphite after 100 min ball milling which confirms the formation of few layer graphene. It can be seen from the diffraction pattern, fig.7 d, that the inner circle is made up of six bright spots indicating hexagonal crystal structure. The intensity of spots in outer circle is different than that of spots of inner circle also many of these spots are diffused which is clear an indication of presence of multilayer graphite structure and of no single layer graphene [10].

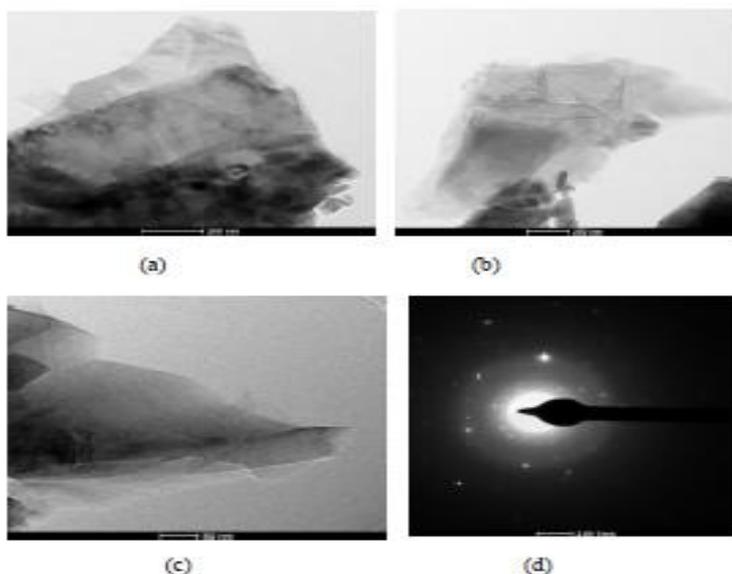


Fig 8 a, b, c shows TEM image of graphite after 100 min milling with Zr balls
d) Diffraction image of graphite after 100 min milling with Zr balls

Graphite sheets produced with Zr balls retained its platelet morphology regardless of milling time (fig 8 a, b, c) and suggesting comparatively slower rate of formation of graphite nano sheets[11]. This can also be confirmed from the diffraction pattern, in which the intensity of dark spots of inner and outer circle are completely different and many of these are diffused. Hence we concluded here that the graphite nano powders prepared using SS balls are more suitable as reinforcement and hence used for making composites and for further studies.

3.3 Synthesis of composites

For synthesizing composites of Polyaniline (PANI)-graphite-nanosheets we mechanically mixed the constituents using SS balls. This mechanical mixing is carried out in planetary ball mill to attain homogeneous distribution. Then the mixture, with different composition, is compressed with 5 tons of load using hydraulic press. Total of six compositions were prepared with increasing 10% graphite by weight percent (from 10% to 60% of graphite), as reinforcement. Same procedure is followed for all three powders of graphite, milled for three durations(viz. 100min, 200min and 300min), to finally get total of 18 different composites,(3 milling duration X 6 compositions). These composites were characterized using micro hardness test and electrical conductivity meter.

3.4 Micro Hardness

Hardness of samples was taken using micro hardness tester. 100 g load was applied for dwell time of 15 seconds.

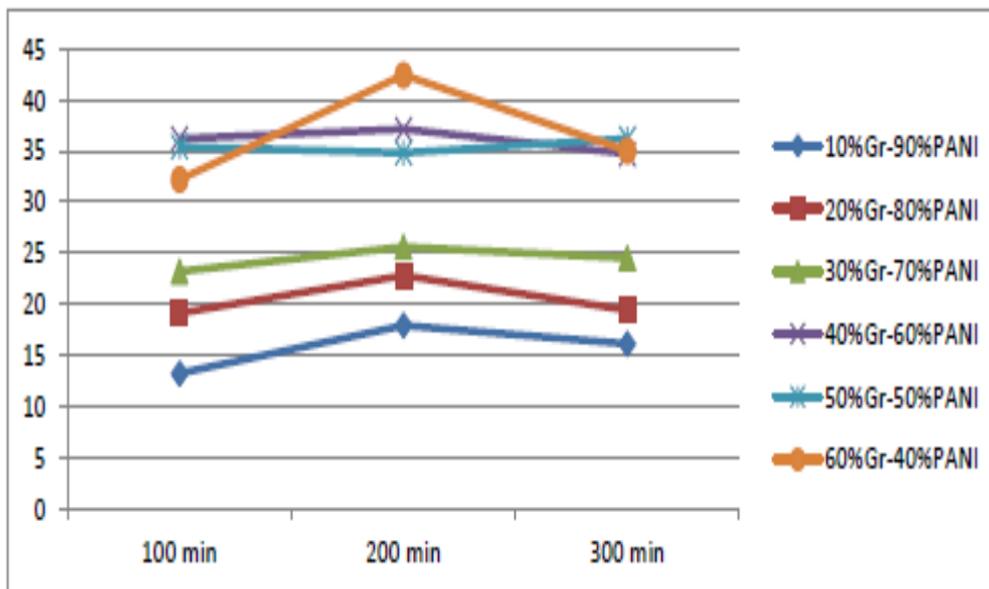


Figure 09: Micro Hardness PANi-Graphite nanosheets composites

These results reveals that for each composition there is considerably higher hardness for 200 min ball milled graphite powder reinforced samples. For 300 min powder sample the hardness is lower as compare to that of 200 min sample but it is greater than hardness of 100 min powder reinforced samples. However with increasing the graphite percentage the hardness goes on increasing. And these values starts from around 15 Hv for 10% graphite reinforced composite and goes on increasing with increasing graphite percentage in composite and for 60% graphite samples it is around 40 HV.

3.5 Electrical conductivity

The electrical resistivity of the composites was measured using four probe method. Conductivities of samples were then calculated using average of resistivity values at three different locations on single sample. The values of conductivities are plotted in figure 10. The possible reasons for variations observed may be attributed to the conduction mechanism of graphite nanosheets which includes two aspects, one the directional electron movement in the graphite layers and other is the electron transition between the layers. On one hand, the PANi conjugated chains offer good conducting paths on the surface of graphite nanosheets layers, which activate more electrons to participate in the

directional movement. On the other hand, the embedded PANi into the space between nanosheets of graphite may cause some conduction between graphite nanosheets. The existence of PANi chains acts like a bridged linkage, which enables the electron to transfer between the graphite nanosheets easily. These synergistic effects leads to the increases of the conductivity of graphite nanosheets/PANi composites observed in figure 10[12].

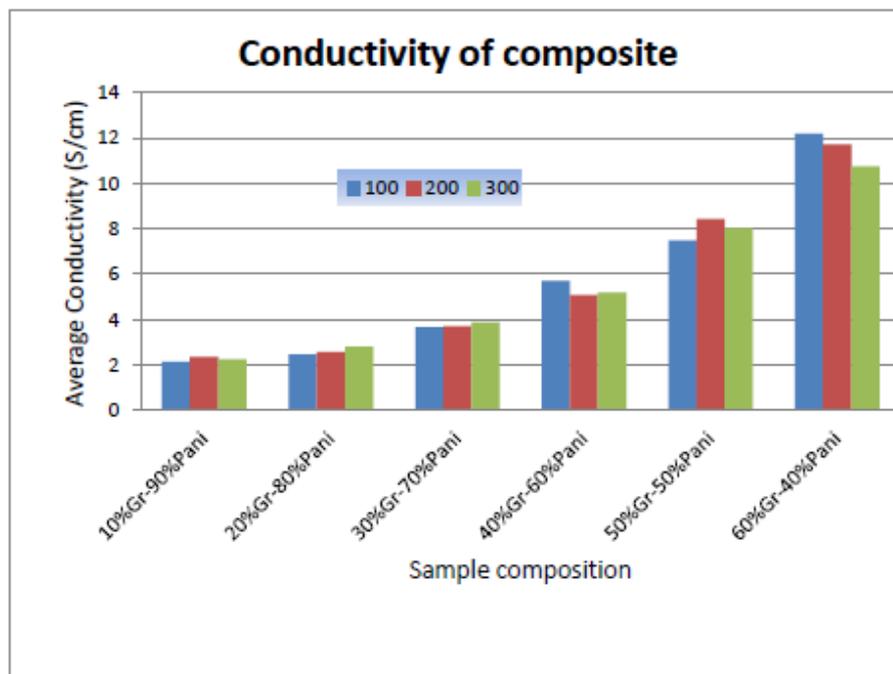


Fig 10 Electrical conductivity of different polymer composites

IV. CONCLUSIONS

- 1) Mechanical milling is the effective way to prepare Nano sheet of graphite. As milling time increases particles becomes smaller and highly aggregated.
- 2) Out of the SS and ZrO₂ balls used for the ball milling, SS balls are found to be effective to produce graphite Nano sheets due to high impact energy.
- 3) As graphite percentage in PANi composite samples increases its hardness and conductivity increases.

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