An Article on CNT - Polymer Composites as Smart Material - As Liquid Sensing Materials

Vivek O Vyas[1]

[1]*Student, Department of Mechanical Engineering, Smt. Kashibai Navale College of Engineering,*
vyasvivek123@gmail.com

ABSTRACT

This paper is a brief review on CNT nano-composites, especially, a wide look on the conductive polymer composites. Electrical and morphological properties of the composites are studied and change of concentration of the CNT as filler material has been discussed with respect to electrical properties. Relation between aspect ratio and percolation threshold is pointed out by comparing them. Some functional properties such as tunneling effect are also overviewed along with the comparison between filler percentage and the resistivity. Parameters affecting the composite properties and various production methods are important in increasing the response time, stability and accuracy of the device which are manufactured using these nano-composites. The basic application of these composites as smart material is thoroughly reviewed and its futuristic application in sensing of various organic liquids and gases has been critically designed and developed into sustainable idea.

Keywords*: Polymer nanocomposites, CNT-composites, Smart material, liquid sensors, etc.*

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1. INTRODUCTION

1.1 CNT CPCs-Carbon Nanotube

CNT and its composite has been one of the most interesting and interesting areas in nanotechnology due to their potential as high-performance and multifunctional materials and wide range of applications. Despite of the properties of CNT but along with the polymer composite it is the most studied topic. From several decades efforts have been taken on their mechanical, electrical (conductive, di-electrical, capacitive), gas barrier and other properties, which provides them a great scope in the sensing elements and applications in various sensing materials [1-3].

So this paper contents a brief on CNT composites, electrical properties of the composites, parameter affecting the composite properties various production methods, designing of the specimen, and its application.

1.2 Introduction to various parts:-

This review paper has been divided in various parts the first part is the introduction which gives the motive and grounds for research in CNT and its composites. Next to it is a general background of the research made with this topic which briefs us on the topics which were focused yet as a research topic. Third section highlights the CNT and its properties which make it an attractive sensing material. Along with polymers and its attractive properties which makes it the best filler material for the composites. The fourth section is on polymer composite and its characterization**.** Fifth one is the sensing mechanism which shows actual working and design of the specimen Sixth part is Change in temperature and other parameters are characterized as mechanical deformation, variation of the percentage of the filler material, conductivity and the di-electric properties. The production methods available according the applications required. Application of CNT as a smart material is the eighth topic. Conclusion & the future outlook in research advance. CNTs along with carbon powder, nanofillers, nanoplates, graphene etc are the best nano fillers for the excellent electrical properties of the composite.

2. BACKGROUND OF THE TOPIC

Lot of fillers when fabricated with the polymers gives good conductive properties [4], wide range of fillers and polymers are available. Frequently used are various metal oxides and carbon materials as carbon nanotube, graphene, carbon black powder etc [5]. Conductivity of the composites can be increased by varying the composition of filler percentage and production processes.

2.1 Reason for Research in Carbon Nanotubes:-

Especially in last decade CNT and its composites has been a good topic in nanotechnology research due its excellent properties as, newer and relevant processes or the production [6] of CNT and its grades are available. Cost reduction is also one of the important factor and processing methods for enhancement of electric and mechanical properties. Hence, exceptional background offers an excellent scope in further research on the composites and its applications as smart materials.

3. ATTRACTIVE PROPERTIES

3.1 Attractive properties of Carbon- Nanotube, Graphene, Nanoplates

CNTs, graphene sheets and nanoplates are more popular due to,

- High aspect ratio
- Low specific gravity
- Excellent mechanical, electrical & di-electrical properties
- Relatively low percolation threshold
- At very low concentration of CNT composite show superior electrical and di-electrical properties [7-9].

3.2 Attractive Electrical Properties of Polymer Composites

Most polymers are not conductive still when are fabricated with conductive fillers give good results in conductivity. This property can be raised with increase in filler content at a critical content level. This observable fact is known as the electrical percolation threshold. From the review of many theoretical and experimental studies (*Pc)* generally decreases with increasing filler aspect ratio [11]. Hence for building an excellent conductive CPCS the aspect ratio must be high. Electrical conductivity is based on conductive network as layers of the filler and polymers are placed offers overall resistance due to tunnelling effect between these conductive layers and the polymers at nano level [6].

4. CPCS (CONDUCTIVE POLYMER COMPOSITE)

A conductive polymer composite is a material made from one or more filler material in a polymer matrix base which is significantly made for the use of combined properties output.

- Filler material is CNT and a polymer matrix.
- As the name it-self suggest that the composite is electrically conductive.
- CPCs with CNT show their unique property: shows low specific gravity with excellent mechanical and electrical and process ability.

This conductive nature shows an exceptional property when exposed to any external environment, shift in temperature, mechanical deformation, presence of organic liquids and solvents gives an electrical response.
By using this property of CPCs and integrating it with external sources liquid sensing devices can be made [11].

4. 1 Effect on conductive property with increasing the filler percentage

As to increase the conductive property the filler percentage can be increased in the polymer but the composites practical formation in more hard the precipitation of the filler starts and mechanical and some other

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properties starts changing which is not desirable for the applications we are looking for. So no matters the percentage be less, important is the distribution of the conductive networks inside the polymer matrix.

Various parameters affecting electrical properties (conductivity) of polymer composites:-

- The electrical properties of the material are dependent mainly on the *morphology* of the composite formed.
- The characterization of the morphological properties is very necessary.

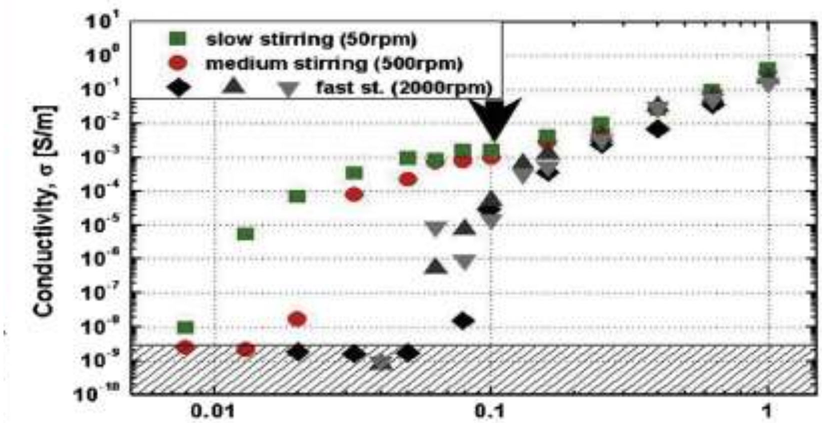

Fig-1: Different conductive network morphology under OM and electrical percolation behavior of CPCs based on MWNT and epoxy. Different processing parameters could lead to significant difference in electrical properties. [12]

4.2 Relations between percolation threshold, conductivity and filler content

A scaling law according to classical percolation theory:

$$\sigma = \sigma_0 (p - p_c)^t$$

Where p_c is the percolation threshold of the CPC, p is the filler content in the CPC; σ_0 is a scaling factor and is the σ conductivity of the CPC [13]. The percolation threshold is predicted to decrease with increasing filler aspect of reported studies in the literature [14, 15]. Ratio this expectation has been confirmed by a number of properties shown in the side.

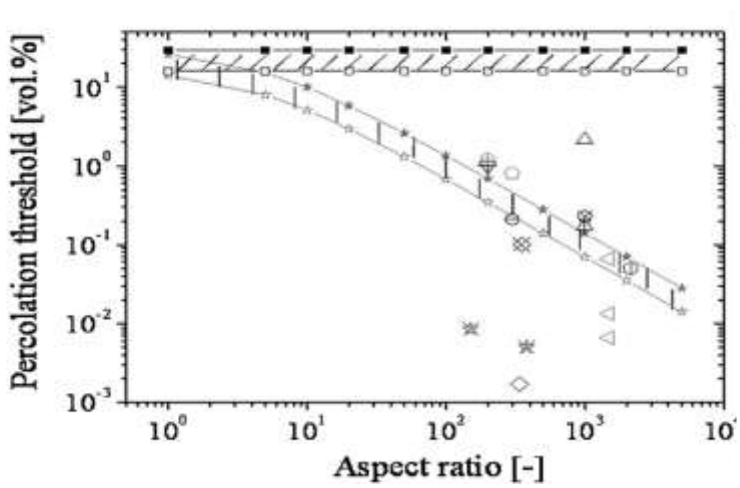

Fig-2: Theoretical electrical percolation threshold versus conductive filler aspect ratio for aligned and isotropic composite systems by various references cited in the work from *Deng et al.* [16]

4.3 Solubility parameter

A solubility parameter was introduced by Hidebrand and Scott, which was defined as the square root of the cohesive energy density. This parameter was divided into allowing dispersive, polar and hydrogen bonding. A critical limit on the solvent molecule size was studied as Ra, further which penetration of the solvent is not possible.

Temperature sensitivity of the solubility parameter was studied. Hydrogen bonding was the most affected parameter. Increasing the temperature decreases the hydrogen bonding factor (17-19).

5. WORKING MECHANISM OF THE SENSING MATERIAL

Diffusion of these organic solvents into the polymer takes place which swells the polymer and thus increases the conducting polymer distance (tunnelling distance) and hence the tunnelling current is lowered. The critical limit for the tunnelling distance is 1.8mm [19] if the distance increases beyond this resistivity will start increasing. For uniform filler material relative change in resistance depends on geometry of specimen, filler content, penetration depth, time provided and temperature of the system. The swelling starts from the surface and to the core hence if sufficient time is given then at the extreme limit it will reach the maximum valve. Designing the sensors the response time should be less along with high accuracy. The conductive filers are in indirect contact hence it becomes discontinuity in conductive flow. With the tunnelling distance among the electrons is also a reason for the resistance [20, 21].

It has been suggested that the interaction between conductive fillers (especially carbon-based fillers) needs to be taken into account during processing [6, 15]. Therefore main objectives of the production are producing the least percolation threshold with the high aspect ratio fillers (CNT, Carbon Nanofillers& graphene) focusing on the linear dispersion or we can say morphological control.

6. PREPARATION OF CPCS

The preparation of the composites is a important process which involves controlling on morphology of conducting network. Appropriate filler material is required with production method which will play an important role in enhancing the electrical properties of the composites. Some of such methods listed over here:-

6.1 Melt compounding

This process is an effective process due to the dispersion of filler material throughout the material rather on the surface. No other reagents or chemical impurities have a chance to precipitate within the composite formed. Huang et al. [22] reported a study on the melt com-pounding of polydimethylsiloxane (PDMS) with MWNTs. Actual change in viscosity was recorded for the quantitative and relatively good dispersion, as concentration goes increasing the time required for uniform dispersion is more providing sufficient time for dispersion. *Villmow et al.* [23] conducted a systematic study on the melt processing of CNT/polymer composites (residence time, filler dispersion).

The processing parameters influencing are listed below:-

1. Increase rotation speed decreased residence time
1. Machine parameters, the design of the screw pro-files can enhance filler dispersion
2. M\aster batch dilution process can be used for low percolation threshold
3. Chemical polarity between the filler and the polymer
4. Compatibilisers or surfactant can be used for interaction between filler and matrix (24, 25-27).
5. Critical mixing time (for high shear stress optimum critical time is required).
6. Shear stress inside the mixer (optimum range due to reduction in aspect ratio).

As melt compounding is an effective and efficient process and more over and conventional process.

6.2. In situ polymerization

In polymer chemistry, in **situ polymerization** means "in the polymerization mixture." There are numerous unstable oligomers (molecules) which must be synthesized in situ (i.e. in the reaction mixture but cannot be isolated on their own) for use in various processes.

One example of this method is protein nano-gels made by the in situ polymerization method. It has tremendous applications for cancer treatment, vaccination, diagnosis, regenerative medicine, and therapies for loss-of-function genetic diseases.

Advantages of this process:-

- Polymer chain and the fillers can be dispersed and grafted on the molecular scale.
- Gives good mechanical and electrical properties
- fabrication of polymers using graphene
- CPCs was obtained directly at the end processing is not required
- Production of thermo set and rubber-based CPCs

It is more difficult to adapt in situ polymerization than melt compounding as a general method for the preparation of CPCs to industry [28-30].

6.3. Solution mixing

Other methods may lead to scalable dispersions, but locally homogeneous dispersion states are difficult to achieve without breaking down the entangled fillers (such as CNTs). Nevertheless, some characteristics of the fillers, such as the sp2 hybridized structure of the Nanotubes, make these fillers insoluble in a common organic solvent.

- Advantage is homogeneous mixture is possible
- This process provides a low threshold percolation than melt moulding.

Functionalisation

Functionalisation on the filler surfaces provides dispersion and strength the mixing. Hence right amount of functionalisation with appropriate type is required. All this is made to make the filler material more soluble in the polymer base [31-33].

7. DESIGN CONCEPTS AND CAPABILITIES

No of designs are proposed according the applications :

- Partially embedded CNTs in polymer
- Arranged in denser network
- Fully embedded CNT in polymer matrix
- ➢ At the place of having a coating fully embedded system is preferred due to its more potential in sensors applications. Various cost efficient and process-ability methods are suggested for the production of fully embedded composite as injection or compressing moulding, blow moulding, and fiber spinning.

The results of this change in environmental stimuli are shown by relative change in resistance. A high change in resistance is observed near the glass transition temperature (Tg). Electrical change in response under mechanical loading is observed. Here tunnelling distance between the individual CNTs was increased and hence increase in resistance was seen. Swelling of the composite occurs due to which increase in tunnelling distance and resistance occurs. Various shapes and design of the CPCs make them more interesting topics.

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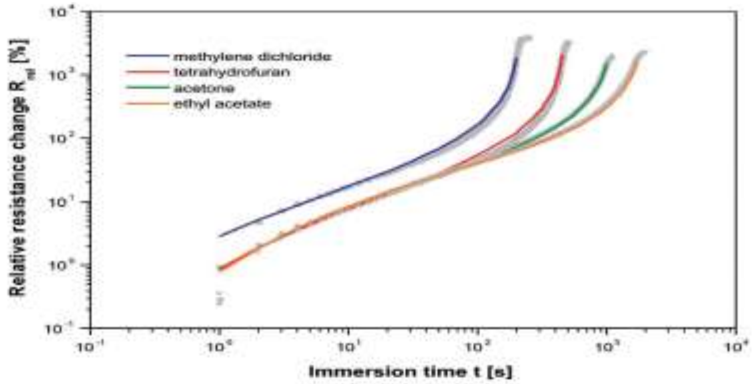

Fig-3: Electrical response characteristics of PC/MWCNT composites during immersion in different solvents, adapted from [23]

8. DESIGN OF SPECIMEN AND SETUP

Specimen is a simple towel like structure. Cloth is integrated with wires and this is provided with the supply voltage and the output readings. So that the readings can be further processed stored and used.

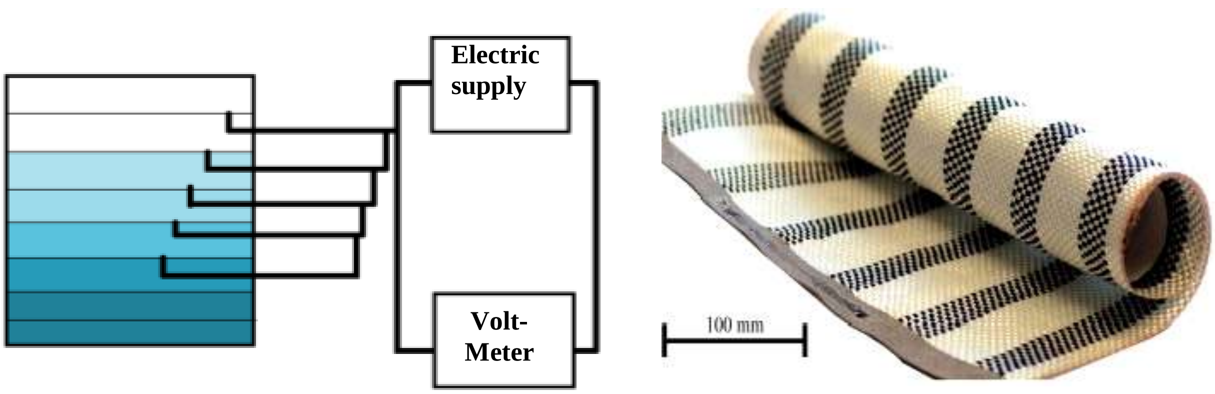

Fig-4: (a) Total setup with a battery supply and a voltmeter for the deflection, (b) simple towel like sample cloth.

9. APPLICATIONS OF CNT BASED COMPOSITES AS SENSORY MATERIAL

Water levels, nuclear power plants coolants, internal burners, detection of *organic gases* including antistatic, electrostatic painting and electromagnetic interference (emi) shielding, CPCs have been investigated for many potential electro active functionalities, including strain/damage, vapour/liquid and temperature sensors, stretch-able conductors, shape memory materials [34] and thermoelectric materials

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10. POTENTIAL APPLICATION FIELDS

10.1 At the Sealing of Containers

Fuel tankers and liquids level inside the tank can be known accurately in digital format and will be betterment for tank services. Fuel storages which are under-ground &other storage tanks can be integrated with this material.

10.2 At Sea Highs

Various organic fuels can be found under sea level. Detection of diesel, petrol & other organic liquids will be easier. A probe can be made & sent deep in sea with its outputs can be noted by the operator. The output can be classified in various ranges for different liquids .The probe can be made in a circular bottle shape which can be used in mines for the detection of flammable gases.

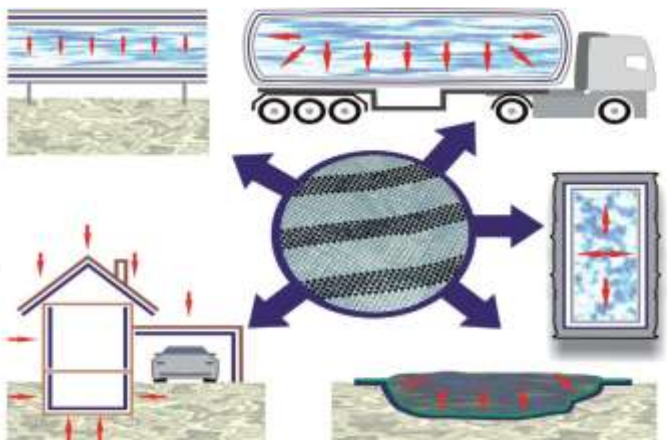

Fig-5: Possible applications of sensory CPC in *Sealing of Containers, water tanks, fuel tanks, nuclear power plant boilers*. [6]

Further scope on the topic:-

- How to increase the response time by doping of various metals?
- Dielectric properties of the material.
- CNT as super capacitors so that the device will be automated.
- Temperature effect on the system.

11. CONCLUSIONS

CNTs when doped with the polymer base forms the conductive polymer composites with excellent stability and mechanical properties. Conductive networks endow CPCs with their electrical properties. In addition, the majority of the resistance in a particular type of CPC is derived from the tunnelling resistance between local conductive networks; therefore, tuneable electrical properties can be obtained by adjusting the conductive networks.

But the main property which makes this type of composites a smart and advanced material is that these conductive nature shows an exceptional property when exposed to any external environment, shift in temperature, mechanical deformation, presence of organic liquids and solvents gives an electrical response and this response can be recorded using a integrated circuits which makes this composite a smart sensing material for many advanced applications. Modifications as increase in content of filler can be done along with change in various processes for the production which can be adopted in order to increase electrical characteristics. This critical content limit is known as percolation threshold which plays a crucial role in sensitivity and accuracy for the sensor device. Therefore CNTs and a variety of polymers can be used as liquid sensing, organic gages detecting material.

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