

# MECHANICAL AND ELECTRICAL PROPERTIES OF CARBON NANOTUBES BASED ACRYLONITRILE BUTADIENE STYRENE NANOCOMPOSITE FABRICATED USING FUSED DEPOSITION METHOD

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## ABSTRACT

A Polymer can enhance its properties by addition of a very small weight percentage of micro or nanomaterials which can tailor of polymer. In this research work, multiwall carbon nanotubes (MWCNTs) were added in percentage ranging from 0.1 to 0.3% by weight in acrylonitrile butadiene styrene (ABS) and a spool in the form of material was prepared for 3-D printing with the help of an extrusion machine. Characterization of these new composites can be done by using scanning electron microscopy (SEM) imaging and electron dispersive X-ray spectroscopy (EDS) to validate effect of the addition of multiwall carbon nanotubes into ABS based nanocomposite. The samples were printed as per the ASTM D638 and ISO 178 standards using dual extruder 3-D printer by fused deposition modelling (FDM). The tensile and flexural tests were performed with and without multiwall carbon nanotubes in the ABS material. The tensile test results in an increase in strength by 21.61% while the flexural test results a decrease in strength by 15.13%. With both of the tests it indicates the increase in brittleness of the composites with increment in the percentage of nanomaterials. Further an electrical conductivity test was performed on nanocomposites with weight percentage of multiwall carbon nanotubes, and have shown significant increase in electrical conductivity with the addition of multiwall carbon nanotubes.

**Keyword** - FDM, Nanocomposite, Characterization, MWCNT, Modelling

## 1. INTRODUCTION

Today objects can be manufactured with Additive manufacturing processes that have changed methodology drastically. It has wide applications in aerospace industry, fashion industry and rapid prototyping industry [1].

A 3-D printing produces parts or products with addition of successive layers of material on a platform by using bottom to top approach. [2] A material can be a thermoset or thermosetting plastic with addition of certain additives such as CNTs (SWCNTs/MWCNTs) or graphene. For 3D printing most common and famous form is thermoplastic extrusion, known as fused deposition modelling (FDM). [3] Addition of CNTs and other structured additives improve

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functionality of 3D printed composite parts. Polymer composites and their development as a material for 3D printing are of greatest interest among all researchers and industry specialists. Carbon nanotubes are known for their mechanical, electrical, and thermal properties, which initially makes them a suitable candidate to integrate into 3D printing polymers. Though this technology has so many widespread uses, still it is not the primary way to produce objects in the world. Though a lot of research is being done on this technology, still many hurdles remain to make this technology more accessible and widely accepted. To make this happen additive manufacturing must have materials with wide range of properties to print with. There should be a material which is lightweight but has high strength with good electrical properties. MWCNTs were purchased from the vendor for this experimental analysis and the SEM image of the MWCNTs is shown in Fig. 1.

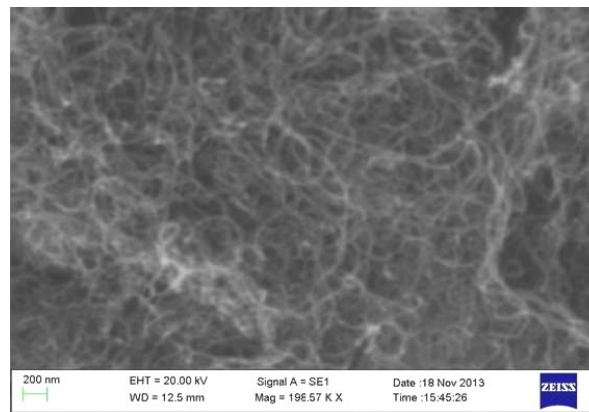


Figure 1. MWCNT an image through Scanning Electron Microscope

Till now various conductive nanoparticles have been used in 3D printing for product development, such as carbon black, Graphene oxide, reduced Graphene oxide, Graphene and multi or single carbon nanotubes. However, very limited studies have been focused and products are developed on the production of Nano composite filament feedstock for FDM. Zhang et al. reported the resistivity of composite filaments with a diameter of 1.75 mm used for 3D printer with reduced grapheme oxide and Poly lactic acid of 0.21 W cm (6 wt. % reduced grapheme oxide used), along with the superior mechanical properties of FDM parts. Zhang et al. reported the effect of 15 wt. % of Carbon Black when used for the resistivity variations of composite ABS feedstock filaments (about 2900 W cm) and characterized the resistivity of 3D-printed parts under various FDM parameters.[4] Wu et al. dispersed up to 3 wt. % multi-walled carbon nanotubes (MWCNTs) in poly hydroxyl alkanooate to produce feedstock filaments but the resistivity of filaments have not been reported as defined result. Wei et al. were able to produce 3D printed parts with 5.6 wt. % of Graphene Oxide in ABS matrix but they did not investigate electrical or mechanical properties of product. Gnanasekaran et al. reported on the 3D printing with polymer Nano composites consisting of single wall carbon nanotubes (SWCNTs) and graphene-based poly butylene terephthalate, finding that 3D-printed objects filled with SWCNT have better conductive and mechanical properties and better performance than those filled with graphene when compared.[5]

Ultrahigh molecular weight polyethylene (UHMWPE) has been processed with MWCNTs and extruded to produce filaments [6]. However, it is not feasible to produce UHMWPE filaments by conventional extrusion due to the high Weissenberg effects [7] that would likely affect the

flux during extrusion both for filament production and 3D printing. An alternative would be to use the gel-spinning technique [8] in which the polymer is dissolved and spun. The addition of MWCNTs can be problematic as they tend to aggregate during the solvent evaporation stage, but the problems were addressed by using a range of techniques including sonication, melt mixing, and extrusion [6].

Grafting of single wall carbon nanotubes SWCNTs to poly (L-lactic acid) has been investigated [9] but so far MWCNTs are dominant, possibly due to their increased metallic character. However, Vatani et al. reported the fabrication of a highly stretchable sensor by dispersing 1wt% SWCNT (average diameter 1.5 nm, length 1–5 micrometer) in a matrix of a blend of two photo curable monomers (cyclic trimethylolpropane formal acrylate and acrylate ester) [10]. The monomers/SWCNT composite was printed using direct writing into a polyurethane substrate on which the monomers were photo cured. The wires sustained strain up to 90% elongation and resistivity change increased proportionally with the strain.

## 2. EXPERIMENTATION

### 2.1 Experimental Techniques

The research involved fabrication of composite material, characterization of the new material, printing the samples for testing and finally testing for the mechanical and electrical properties of this material. To achieve this, firstly the composite material was prepared at the facility provided by Solid space technology in Nashik, India.[11] Solid space filament extruder had double screw setup to ensure optimum mixing of material. A mixture of ABS and MWCNTs in various ratios was inserted into the hopper of the machine which then gave out a filament of 1.75mm diameter wound around a spool as shown in Fig.2 The extrusion temperature used in this machine was 178°C [12].



Figure 2. Solid Space extrusion machine setup

### 2.2 Test Specimen Preparation

After extrusion process, prepared spool was installed in a 3-D printer (ACCUCRAFT i250D) [13] to print and test samples for tensile and flexural test. The tensile test specimens were printed in accordance to ASTM D638 [14] standard as shown in the fig. 3 and flexural test specimens were printed in accordance to ISO 178 [15] standard as shown in fig. 4. These standards were chosen as they were specifically chalked out for plastics testing.

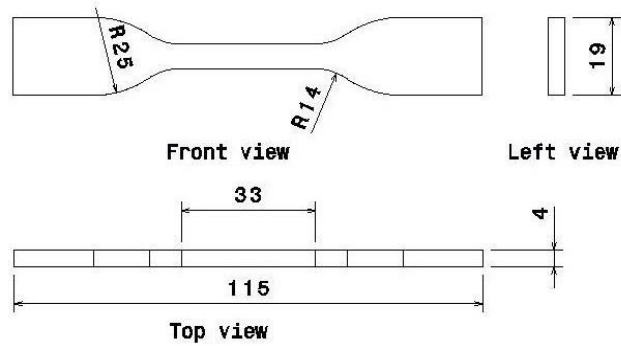


Figure 3. Test specimen for tensile test in accordance to ASTM D638. [5] (All dimensions are in millimeter)

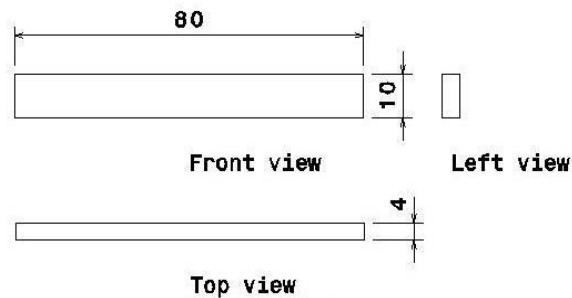


Figure 4. Test specimen for flexural test or three point bending test in accordance to ISO 178. [6] (All dimensions are in millimeter)

The printed samples were then tested for tensile and flexural test in a universal testing machine (Shimadzu AGS-X 100KN) available at VJTI, Mumbai as shown in fig. 5. The failed samples were then taken for Scanning Electron Microscopy (SEM) imaging at Central Institute for Research on Cotton Technology (CIRCOT), Mumbai and for Energy Dispersive X-Ray Spectroscopy (EDS) analysis at Indian Institute of Technology (IIT), Bombay. The filament was also tested for electrical conductivity using a high resistance meter by H.P. (4339B). The filament of one meter length was used as a test specimen and the results were taken



Figure 5. Shimadzu AGS-X 100KN

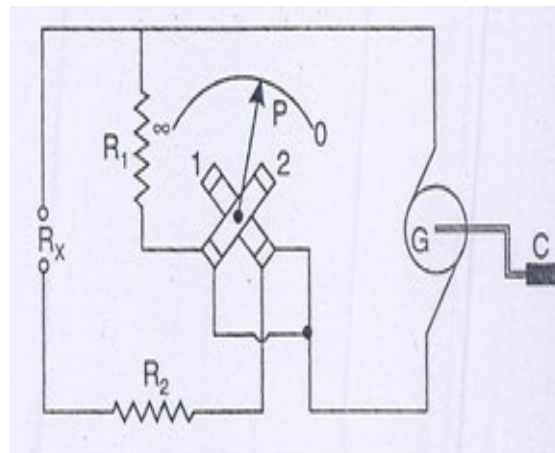


Figure 6 Simplified Circuit diagram of High Resistance Meter

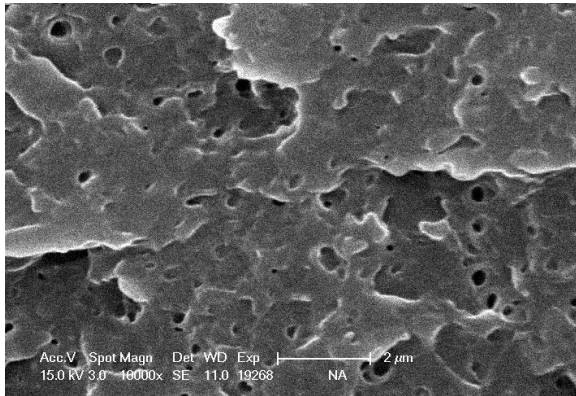
at multiple voltage readings. Test setup is as shown in the fig. 6.

### **3. RESULTS**

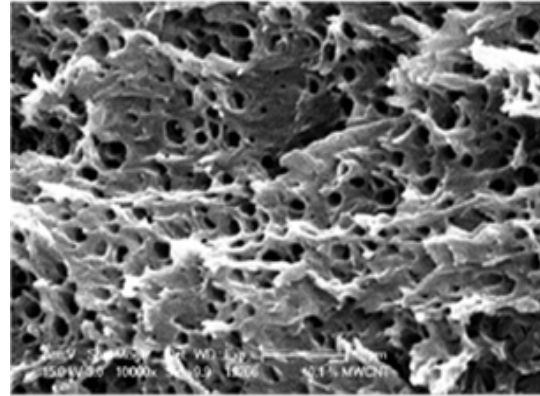
#### **3.1 SEM Characterization**

The characterization report by SEM imaging clearly shows the addition of MWCNTs Nano powder in ABS material as there is significant difference in the images taken for natural ABS material and composites of ABS and MWCNTs are shown in Fig. 7 a, b, c, d and e respectively. The rough and more fracture surface from the SEM imaging clearly indicate that the additional adhesive bond has been created by MWCNTs in the ABS. The rough surface shows the strong adhesive bonding before failure in the tensile testing with presence of MWCNTs is more clearly shown in Fig.7e. The SEM images of MWCNTs is shown in the Fig. 7f and this can be clearly observed in the failed specimen cross-section view in the Fig. 7e.

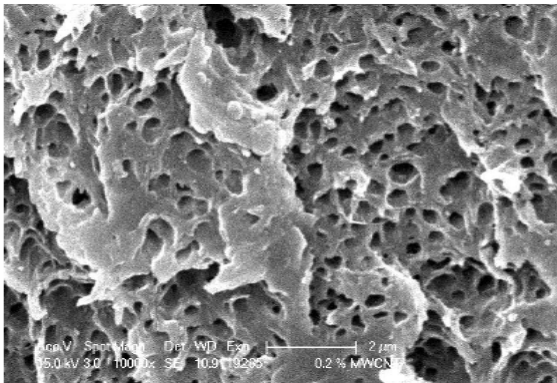
The failure of the specimens has been seen under the SEM to visualize and see the correlation of strong adhesion bond due to addition of MWCNTs in different weight %. However Transmission Electron Microscopy (TEM) images can give better resolution to see the MWCNTs in the nanoscale images. TEM images are not so far obtained.



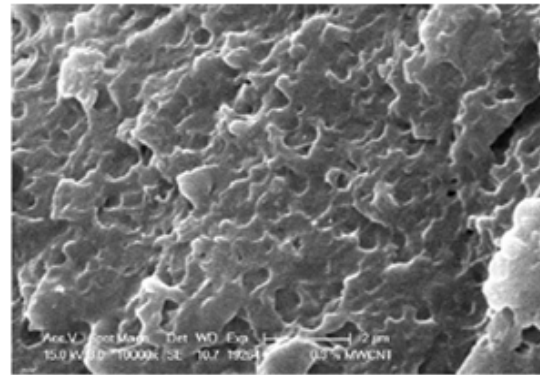
a) Natural ABS



b) 0.1% by wt. MWCNTs and ABS composite

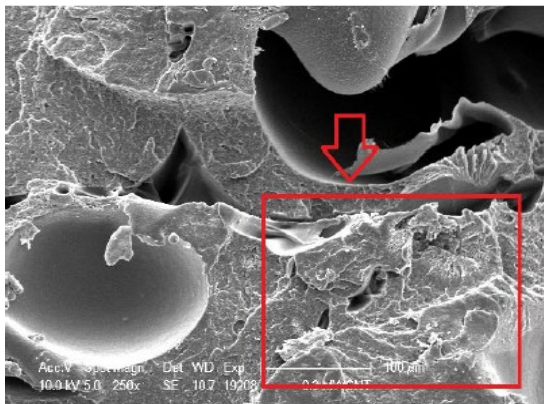


0.2% by wt. MWCNTs and ABS composite

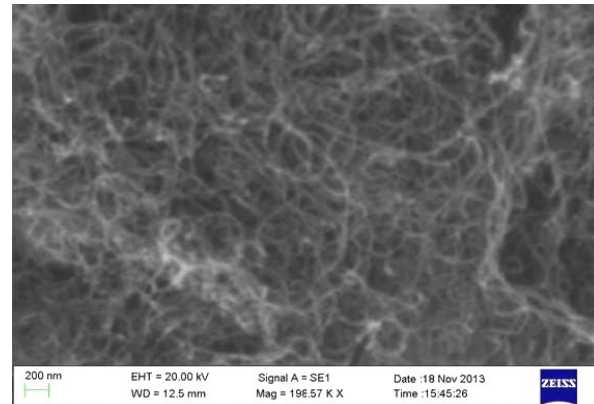


d) 0.3% by wt. MWCNTs and ABS composite

c)



e) Presence of MWCNT



f) SEM images of MWCNTs

Figure 7. SEM images of ABS and MWCNTs with different wt. %

### 3.2 Energy Dispersive X-ray Spectroscopy (EDS Characterization)

Spectral analysis was also performed to find out the percentage of chemical elements in composite material. For this purpose Energy Dispersive X-ray spectroscopy (EDS) was performed. Its report for composition for various elements is given in Table I, II, III and IV respectively.

Table 1: Elemental composition of natural ABS.

<b>Element</b>	<b>Weight %</b>	<b>Atomic %</b>
C K	69.53	73.46
N K	25.77	23.35
O K	3.70	2.94
P K	0.18	0.07
Ni K	0.81	0.18
<b>Total</b>	<b>100.00</b>	<b>100.00</b>

Table 2: Elemental composition of 0.1% by wt. MWCNTS and ABS

<b>Element</b>	<b>Weight %</b>	<b>Atomic %</b>
C K	74.70	77.99
N K	20.81	18.63
O K	4.23	3.32
P K	0.07	0.03
Ni K	0.18	0.04
<b>Total</b>	<b>100.00</b>	<b>100.00</b>

Table 3: Elemental composition of 0.2% by wt. MWCNTS and ABS.

<b>Element</b>	<b>Weight %</b>	<b>Atomic %</b>
C K	75.52	79.34
N K	16.89	15.22
O K	6.54	5.16
P K	0.27	0.11
Ni K	0.78	0.17
<b>Total</b>	<b>100.00</b>	<b>100.00</b>

Table 4: Elemental composition of 0.3% by wt. MWCNTs and ABS.

<b>Element</b>	<b>Weight %</b>	<b>Atomic %</b>
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C K	76.41	79.23
N K	21.78	19.37
O K	1.80	1.40
P K	0.00	0.00
Ni K	0.00	0.00
<b>Total</b>	<b>100.00</b>	<b>100.00</b>

### 3.3 Tensile testing

The tensile testing was done over 3D printed specimens and their stress versus strain characteristics were found out until failure occurs. The failure of specimen under tensile loading is shown in the Figure. 8 for the Natural ABS specimen and a typical failure of the specimens with weight percentages of MWCNTs for 0.1, 0.2 and 0.3 wt. % with ABS respectively.

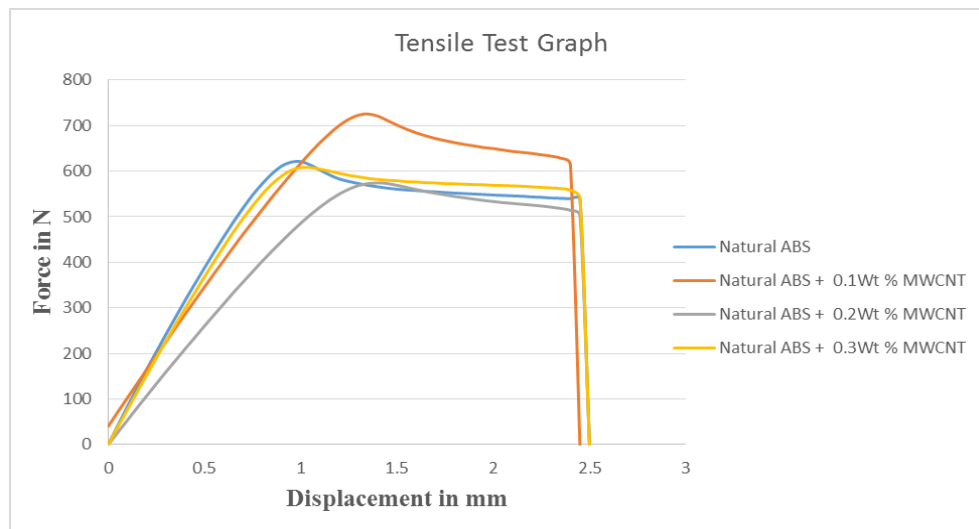


Figure 8. Force (N) vs Displacement (mm) response of the specimen for 0.1 to 0.3 wt. % of MWCNTs in tensile test

From the below result table, it is observed that by adding MWCNTs in natural ABS, by 0.1 to 0.3wt. %, there is enhancement in mechanical properties (Tensile Strength) of the material. Its tensile strength is increased maximum by 21.61% for 0.1 wt. % MWCNTs as compared to natural ABS. For 0.2 wt. % & 0.3 wt. % also, there is increase by 12.59% and 9.88% respectively in its tensile strength. Hence more wt. % addition of MWCNTs in natural ABS has shown increase in tensile strength with 0.1wt % of MWCNTs. However addition more MWCNTs have shown decrease in the tensile strength.

Table 5: Comparison of Average Maximum Tensile Stresses

Sample	Maximum Tensile Strength (MPa)	Standard Deviation	% Increase compared with Pure Material
Natural ABS	24.29	0.89	N/A
ABS+0.1wt%MWCNTs	29.54	0.87	21.61%
ABS+0.2wt%MWCNTs	27.35	2.01	12.59%
ABS+0.3wt%MWCNTs	26.69	0.26	9.88%

The specimens failed in between gauge length and cross section of failed area can be observed with rough surface as shown in figure 9.

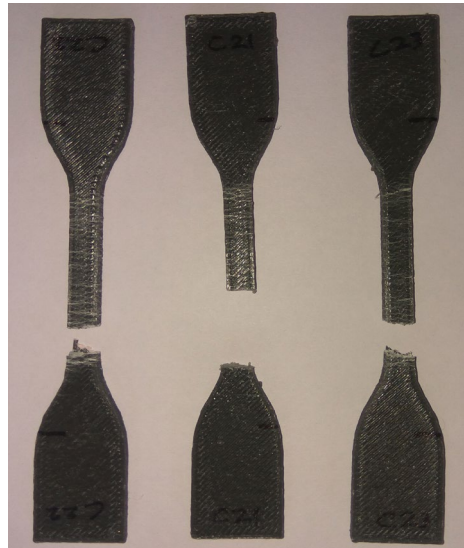


Figure 9. Failed tested samples with 0.2wt. % of MWCNTs in ABS

Deposition of material in fused deposition modelling (FDM) is layer by layer, hence few defects such as voids, air pockets have occurred which are observed and supported by SEM images. Therefore three samples with 0.1 to 0.3 wt% of MWCNTs in the natural ABS materials have different plastic deformation. Also the adhesion bond between the layers gets weaker as the load increases and material failure occurs in tensile testing.

### 3.4 Flexural (three point bend) testing

The flexural or three point bending test was also performed [16-18] and its results obtain for the load Vs displacement relation are shown in the Figure 10 for Natural ABS and for ABS with weight percentage of MWCNTs 0.1, 0.2, and 0.3 respectively. The increase in

MWCNTs weight percentage has shown decrease in the flexural properties due more brittleness in the nanoengineered material.

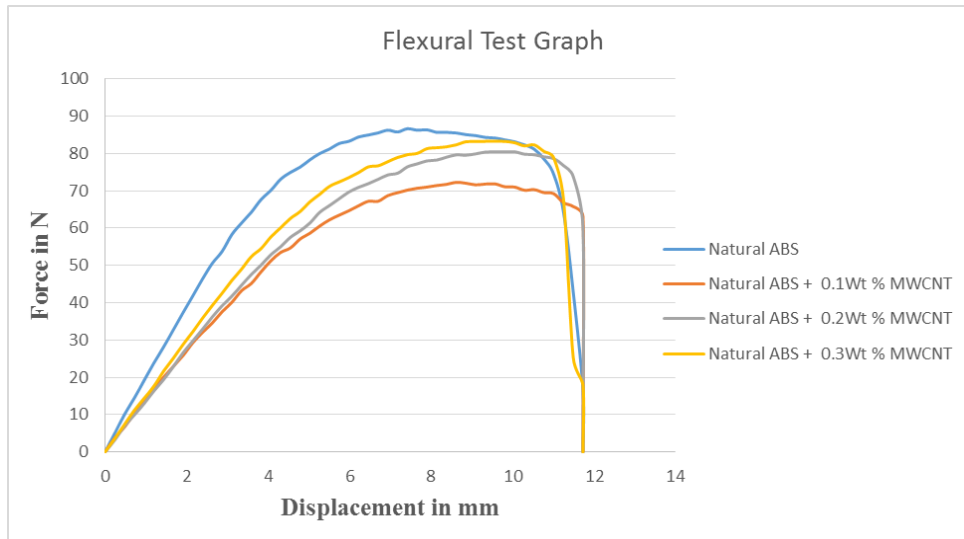


Figure 1. Force (N) vs Displacement (mm) response of the specimen for different wt. % of MWCNTs in flexural test

Table 6: Comparison of Average Maximum Flexural Stresses

Sample	Maximum Tensile Strength (MPa)	Standard Deviation	% Decrease compared with Pure Material
Natural ABS	2.18	0.09	N/A
ABS+0.1wt%MWCNTs	1.85	0.18	15.13%
ABS+0.2wt%MWCNTs	2.11	0.07	3.21%
ABS+0.3wt%MWCNTs	2.07	0.11	5.04%

From the above result table, it is observed that by adding MWCNTs in natural ABS, by certain wt. %, we observed decrease in mechanical properties (Flexural Strength) of the material. Its flexural strength is decreased maximum by 15.13% for 0.1 wt. % MWCNTs as compared to natural ABS. For 0.2 wt. % & 0.3 wt. % also, there is decrease by 3.21% and 5.04% respectively in its flexural strength. Hence more wt. % addition of MWCNTs in natural ABS is decreasing its flexural strength.

### 3.5 Electrical conductivity test

Due to the addition of MWCNTs to ABS, it is observed that electrical conductivity also significantly improved for the polymer composite. The Fig.10 shows the amount of resistance

offered by the polymer composites at various voltages provided. The addition of MWCNTs to ABS also affected the conductivity of the polymer.

$$\rho = \frac{RA}{L}, \quad \sigma = \frac{1}{\rho}$$

Where,  $\rho$  = resistivity, A = cross sectional area, L = length,  $\sigma$  = conductivity, Siemens/meter (S/m)

Table 7: Conductivity of Tested Samples at 15volts

Sample	Conductivity, $\sigma$ (S/m)	% Increase compared with Pure Material
Natural ABS	$1.5455 \times 10^{-8}$	N/A
ABS + 0.1wt. % MWCNTs	$1.6832 \times 10^{-8}$	8.91 %
ABS + 0.2wt. % MWCNTs	$7.1558 \times 10^{-8}$	363 %
ABS + 0.3wt. % MWCNTs	$9.9462 \times 10^{-8}$	544%

### 3.6 Discussion

SEM imaging shows that MWCNTs were successfully assimilated in ABS material. This result was further cemented by element spectroscopy analysis by EDS spectroscopy as it clearly indicated an increase in carbon percentage as MWCNTs purely content carbon. Tensile test analysis shows significant increase in strength by almost 22 % with 0.1 % wt. of MWCNTs. Also it must be noted that pure ABS sample failed with large amount of plastic deformation while with increase in percentage of MWCNTs the brittleness of the composite also increased which in most situations can be considered as a downside. On the other hand flexural test showed a decrease in strength by almost 15 %. But flexural test also confirmed a random increase in brittleness with increase in MWCNTs percentage.

As mentioned in the start of this research work MWCNT's strength is about 90GPa along its layer. But clearly this strength was not achieved in the tests. Many reasons can be attributed to this result. All these reasons will be discussed below.

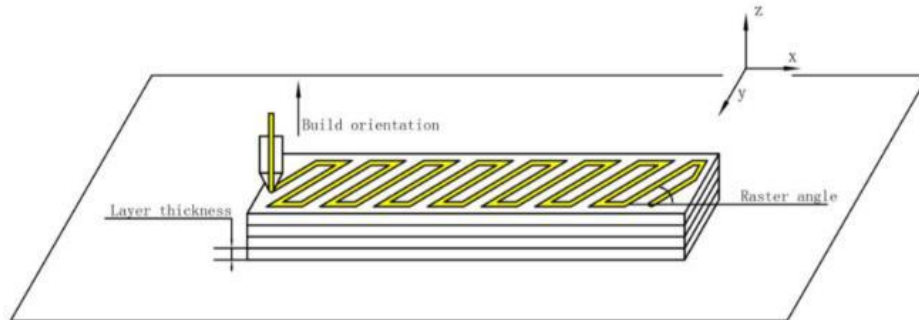


Figure 11. Direction of deposition of material in a 3D printer [3]

While observing the failed specimen it was noted that many samples failed along a 45° angle to specimen's longitudinal axis. It must be noted that sample is printed at 45° angle as it is the standard way of printing according to the infill pattern of G-codes of a 3-D printer. It hints that sample may not have failed because of breaking of layers but by breaking the bond between two layers. Another reason for a premature failure can be that the MWCNT's super strength is

along its layer. When it is added in a polymer its 2-D strength is unable to give high strength in a 3-D polymer.

The electrical conductivity test on the composite material shows an increase in electrical conductivity. This is quite improvement in the properties of the nanocomposites. But again if it is compared with the conductivity of MWCNTs, the increment in composite is miniscule. This can be attributed to the imperfections of FDM process. There are more chances of forming of air bubbles in the samples, which is an insulator. Also the direction of printing of samples is not in the direction of flow of current.

#### **4. CONCLUSIONS**

The result shows a significant increase in mechanical and electrical properties of the composite of ABS and MWCNTs nanomaterial. The increase in conductivity opens up an opportunity of application of 3-D printing in printing of electrical circuit boards. The 3-D printed samples showed an increase in strength and stiffness characteristics. This property can be used in printing of strong and intricate parts with the help of 3-D printers which may not be possible with conventional material or too costly to be done by any other process. Thus, it has potential applications in aerospace industry. Also these polymer nanocomposites are perfectly compatible to use with a 3-D printer as they offered very smooth functioning and tailor the properties of the nanocomposite with controlled parameters during deposition of the layer by layer.

In Summary, the tensile test showed an increase in strength by 22% and while the flexural test showed a decrease in strength by 15% with addition of 0.1% wt. of MWCNTs. With increase more weight percentage of the MWCNTS in natural ABS has further shown the decrease in tensile and flexural properties of nanocomposites of ABS. Both of the tests confirmed the increase in brittleness of the nanocomposites with increment in the percentage of MWCNTs. With addition of weight percentage of MWCNTs in the natural ABS have shown an increase in electrical conductivity due to the presence of MWCNTs in the nanocomposites of ABS.

#### **ACKNOWLEDGEMENT**

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