ABS Nano Composite Materials in Additive Manufacturing

Eshwar Reddy Cholleti[1], Ian Gibson[2]

[1] M.Tech Thermal Engineering, Co - Founder of 3D Srishti Pvt Ltd, Telangana, India.

[2] Professor, Head of School at Deakin University, Highton, Victoria, Australia.

Abstract:

The aim of this paper is to present test results conducted on Multi walled carbon nanotubes (MWCNT) coated ABS (acrylonitrile butadiene styrene), multi wall carbon nanotubes dispersed in ABS resin in comparison with conventional ABS filament for improved materials properties and present possible ways of using nanocomposites materials in Additive Manufacturing (AM) processes. The usage of nanocomposites materials in AM helps to achieve superior material properties and to manufacture complex structures which are not possible to fabricate by conventional methods of manufacturing that allow optimizing the component's weight, shape and strength. Our team 3D Srishti is a group of researchers are exploring the ways of using Nanocomposites, which is broadly classified in to Polymer based nanocomposites and non-polymer based nanocomposites in several AM processes, by using different combinations of nanocomposites, we can achieve precise control over the optical, thermal, electrical, magnetic and mechanical properties of the 3d printed objects by controlling the placement and assembly of nanomaterials during the fabrication process. AM enable to reduce waste by recycling old materials, it reduces transportation, manufacturing costs, AM totally revolutionize consumerism, by promoting sustainable manufacturing.

Key words: Nanocomposite Materials, Additive Manufacturing, Polymer based, Non polymer based, Multi Walled Carbon Nanotube (MWCNT), 3D Srishti.

1. Introduction

Additive Manufacturing (AM) is a novel technology, only three decades old, colloquially known as 3D printing and formerly known as Rapid Prototyping (RP), AM is defined by the American Society for Testing and Materials (ASTM) as "a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies" [1].

AM enables us to manufacture complex structures which are not possible to fabricate by conventional methods of manufacturing that allow optimizing the component's weight, shape and strength. AM consists of several processes like Vat photo polymerization, material jetting ,binder jetting, material extrusion, powder bed fusion, sheet lamination, direct energy deposition, however, each process has its

own limitations as each AM process caters only limited materials, this barriers can be overcome by using nanocomposite materials.

A nano-composite is described as a material that consists of a matrix and a disperse nano-particulate that induces change to its overall macroscopic properties. Nano composites are broad range of materials consisting of two or more components, with at least one component having dimensions in the nm regime (i.e. between 1 and 100 nm), Nano composites are broadly classified in to polymer based nanocomposites and non-polymer based nanocomposites, this materials helps to achieve superior material properties when compared with macro composites [2,3].

Our research on Nano Composite materials application in AM, aims to explore the possible ways of using nanocomposite materials in each processes of AM, The narrow choice of materials used in Additive Manufacturing (AM) remains a key limitation to more advanced systems. Nanocomposites offer the potential to advance AM materials through modification of their fundamental material properties. The expansion of nanomaterials to polymers can result in a huge material property changes, as well as help with making completely new composite functionalities, by using different combinations of nanocomposites, we can achieve precise control over the optical, thermal, electrical, magnetic and mechanical properties [1-4] of the 3d printed objects by controlling the placement and assembly of nanomaterials during the fabrication of objects.

We fabricated multi wall carbon nanotubes dispersed in ABS resin with following proportion Acrylonitrile Butadiene Styrene Terpolymer 80% resin, MWCNT 15%, Proprietary Dispersion Additive 5% which is made by herbal extracts, we spray coated ABS with 5 wt % of MWCNT and compared with conventional pure ABS filament, we found enhanced mechanical properties in spray coated ABS filament compared to CNT dispersed in ABS resin and normal ABS filament.

Nanocomposite materials usage in AM opened avenues for wide variety of industrial applications like Aerospace, Automotive, Consumer Products, Industrial Machines, electronics, medical products, architecture, arts, and forensics, AM enable to reduce waste by recycling old materials, it reduces transportation, manufacturing costs, AM totally revolutionize consumerism, by promoting sustainability in manufacturing [5-7].

2. Application of Nanocomposites in different processes of AM

The combination of Nanomaterials and AM offer new opportunities in nanocomposites, adding nanomaterials such as carbon nanotubes, nanowires, and quantum dots to host matrices such as polymers, metals, and ceramics via AM has the potential to enable greater capabilities in nanocomposites production. This union of technologies could offer clear advantages by the manipulation of fundamental material properties in objects through nanomaterials, that can possess customized geometries, reduced delay between design iterations, single tool production, and increased parts integration.

Past research has demonstrated promising results on incorporating nanomaterials to AM. Two ways to introduce nanomaterials into a 3D print job are: (1) 3D printing of the host matrix material with intermittent stoppages of the batch print job and introduction of nanomaterials automatically or manually, and (2) Pre-mixing of the nanomaterials into the host matrix, followed by 3D printing of the nanocomposite mixture as a complete part. Adding nanomaterials can improve mechanical properties,

increase thermal and electrical conductivity, lower sintering temperatures, and affect dimensional accuracy. This fidelity of control would offer a powerful toolbox in routine 3D object production.

To achieve control of material properties requires us to go beyond process control issues of nanocomposites. AM methods have their own limitations such as nozzle clogging, aggregation within printing media, rough surface finish of printed parts, etc. when nanoparticles are applied with the respective printing media. Fundamental questions must be answered before nanocomposites can be routinely produced via AM - e.g., what nanomaterials can be applied in what AM processes, What measurement steps are needed to ensure homogeneity, or in the case of gradient materials, controlled positioning of the nanomaterials.

Metal Nanoparticles helps decreases in sintering temperature, improves density, decrease shrinkage and distortion and provides electrical conductivity. Carbon nanomaterials will increase in tensile and fracture stress, parts more brittle, rough final surfaces, decrease in density, and significantly improves thermal and electrical conductivity, increase in cell proliferation rate. Ceramics and semiconductor nanomaterials will increase in tensile strength and modulus, parts stiffer but more brittle (Silica), enhanced sintering characteristics (Alumina).

By using nanomaterials in AM process there are several challenges like agglomeration of nanomaterials in printing media, this can be avoided by proper functionalization with organic linker molecules. Cure depth can be affected by the presence of nanomaterials in Stereolithography, possible solution is by finding suitable material for a given wavelength of the UV light source. Nozzle clogging can be avoided by determining ideal composition with high concentration of nanomaterial that could flow freely through the nozzles. Porosity of final parts printed using nanomaterials is higher compared to parts printed without nanomaterials in Laser Sintering, the possible solution is by synthesis of core-shell structures in which the core is nanomaterial, the shell is printing material can improve density of final parts [10].

Work in nanocomposites reinforcement for SL resins has also produced promising results. An approach to improve the mechanical properties of an epoxy based resin by interrupting a build and embedding nonwoven fibre glass plies into the cured part showed an improvement in tensile strength.

Graphene is an atomic-scale honeycomb lattice made of carbon atoms. Graphene is undoubtedly emerging as one of the most promising nanomaterial because of its unique combination of superb properties, which opens a way for its exploitation in a wide spectrum of applications ranging from electronics to optics, sensors, and biodevices. For instance, graphene-based nanomaterials have many promising applications in energy-related areas. Just some recent examples: Graphene improves both energy capacity and charge rate in rechargeable batteries; activated graphene makes superior super capacitors for energy storage; graphene electrodes may lead to a promising approach for making solar cells that are inexpensive, lightweight and flexible; and multifunctional graphene mats are promising substrates for catalytic systems.

Additive manufacturing (AM) has attracted a lot of interest lately. While different types of materials can be used in AM, their properties, such as strength, electrical conductivity and thermal conductivity typically have inferior properties compared with conventionally manufactured counterparts due to the

anisotropy caused by the layer-by-layer approach. Nanoparticles, such carbon nanotubes (CNT) are of particular interest for incorporation into AM media because of their unique properties and their scope of increasing strength is considerable [1,3,9,10].

3. Experiment

In this work a comparative study on carbon nanotubes (CNT) spray coated ABS (acrylonitrile butadiene styrene), multi wall carbon nanotubes dispersed in ABS resin and conventional ABS filament, we observed improved material properties due to addition of CNT and proprietary adhesive.

3.1 Mechanism of MWCNT Dispersion

''Nanodirekt'' is an approach involving the dispersion of nanomaterials in water or solvents followed by a direct addition of this homogeneous dispersion into the polymer melt. The dispersing medium will evaporate immediately and the nanoparticles will stay finely dispersed in the polymer matrix. This method ensures that the dry nanofiller are not fed directly into the extruder eliminating potential health hazards associated with handling of Nano fillers. MWCNT are dispersed along with proprietary dispersion additive and stirring simultaneous to avoid agglomeration, disintegration of agglomerate fractions weakened by the infiltration process and shear forces into small fractals by mechanisms of erosion and/or rupture followed by their distribution in the additive host (Figure 1).
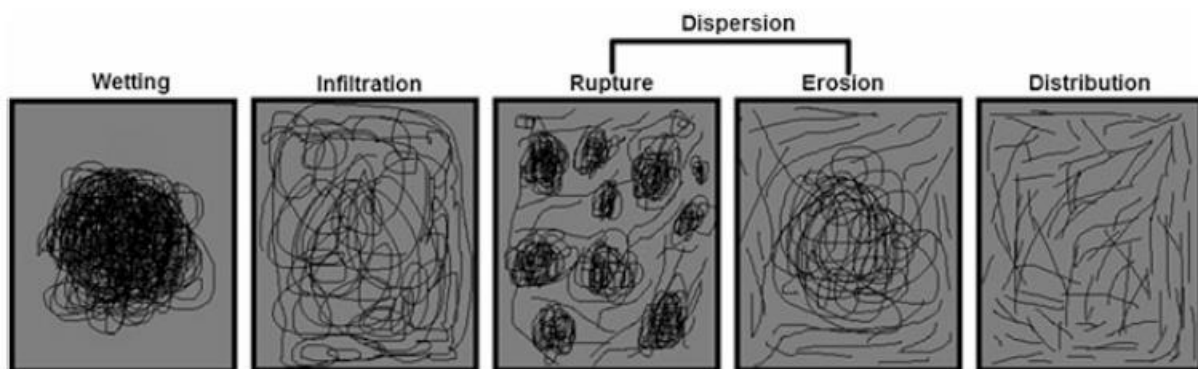

Figure 1: Mechanism of CNT dispersion.

Incorporation of processing additives is a simple and economical strategy for enhancing MWCNT dispersion in thermoplastics. The addition of peroxide during twin-screw compounding led to a substantial improvement in the quality of MWCNT dispersion in ABS owing to the reduction in ABS melt viscosity, this facilitates better melt infiltration into the agglomerates, reduction in their interfacial tension between ABS and MWCNTs leading to better melt wetting of the agglomerates, and surface functionalization of carbon nanotubes resulting in weakening the intra-filler attractive forces. Better wetting and infiltration of the MWCNTs by polyethylene glycol resulted in a significant improvement in MWCNT dispersion in ABS.

3.2 Incorporation of MWCNT with ABS resin

The level of CNT dispersion visible on the composite morphology is a direct function of the type of polymer and CNT employed the processing approach and the process factors. The morphology and therein the macroscopic properties of the composite are dictated by the thermo-mechanical history during processing. Several processing methodologies such as solution casting, melt mixing, solution mixing, different methods of in situ polymerization of the monomer in the presence of CNTs, coagulation spinning, mechano-chemical pulverization, solid-state shear pulverization, electro spinning etc. have been adopted for the synthesis of polymer-CNT composites.

Owing to its simplicity and adaptability for a commercial scale up melt mixing and compounding seems to be the most commonly employed approach for thermoplastic polymer/MWCNT nanocomposites. This method is most suitable for polymers that cannot be processed with the solution processing approach owing to its inability to dissolve in commonly employed solvents. The higher magnitude of shear during the melt mixing process facilitates the breakup of the CNT agglomerates followed by simultaneous dispersion and distribution in the polymer melt. For a melt mixing process to give optimum dispersion quality optimization of all the process parameters like the screw configuration, screw speed, throughput/ residence time, barrel temperatures, filler feeding position etc. is imperative.
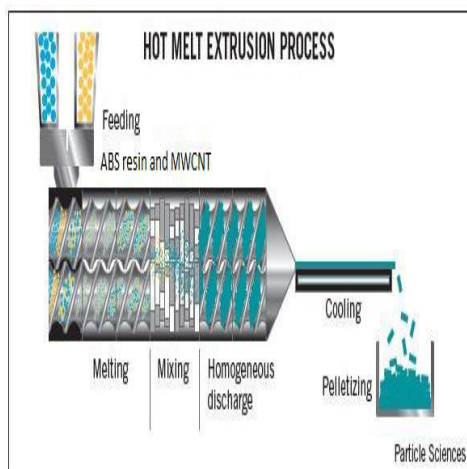

Figure 2: Hot melt extrusion process.   **Figure 3:** ABS dispersed with MWCNT pellets.

Weight % = weight of substance (solute or solvent) weight of mixture ×100%

In this hot melt extrusion process the 80% of ABS resin mixed with 15% of MWCNT dispersed in water, added with 5% of proprietary dispersion additive is introduced in to melting chamber, mixed homogeneously in mixing chamber, the homogeneous mixer is discharged through nozzle and cooled to form pellets as shown in Figure 2, and at the end ABS dispersed with MWCNT pellets are obtained finally as shown in Figure 3.

3.3 Filament production

The ABS incorporated MWCNT pellets are fed to filament maker through pellet hopper. The pellets are passed through screw driven by screw drive motor are melted at heat chamber, and extruded through nozzle to form filament in required diameter. In this process we used 1.75 mm nozzle as a result we obtained the required ABS dispersed with MWCNT filament.
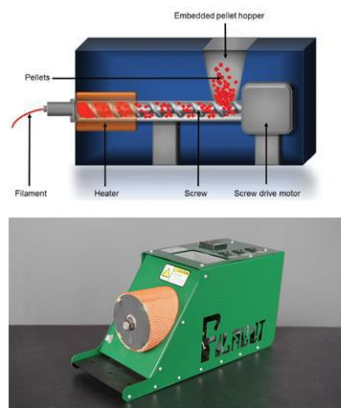

Figure 4: Diagram of a filament maker and a picture of the 'Filabot – Original' used for producing MWCNT – ABS Filament.
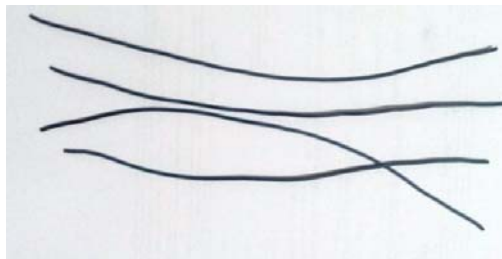

Figure 5: MWCNT - ABS filament.

MWCNT exhibits a range of exceptional qualities including flexibility and conductivity. 3D printing filaments augmented with MWCNT have the potential to enhance the manufacturing process of strong conductive composites. There are many applications of these carbon nano structured additives in 3D printer filaments including sensors, trackpads, electromagnetic, and RF shielding.

3.4 MWCNT COATING AND MICROWAVE SINTERING TO FUSE ABS FILAMENTS

The 3-D printing enables us for easy prototyping, manufacturing capabilities are hindered by the weak weld between printed filaments, which often leads to delamination and mechanical failure. We aim to address this need through a novel material processing technique. In this technique, we use carbon nanotubes because of their small size and the way in which those carbon atoms are bounded have some their unique properties in addition to being stronger than steel and more thermally an electrically

conductive than copper, carbon nanotubes have unique response to microwave energy, that is the heat up rapidly. The week interfaces of 3d printed part is welded with carbon nanotubes, by exposing to microwave energy, for few seconds those interfaces heat up rapidly, weld on all those layers together, now the pure polymer doesn't absorb the microwave energy, so it stays cool we do this by taking this original printer ABS filament to coat with carbon nanotube ink, this produces a coaxial filament which can then be fed into a printer, this processes is explained in detail by following steps.

In first step, polymer filament exterior is coated with MWCNTs by spray deposition. (Figure 6). The MWCNT dispersed in proprietary solvent filled in fluid cup of airbrush and coated homogeneously on the surface of ABS filament, the proprietary adhesive solvent enhances the bonding capacity of MWCNT on the ABS filament, when exposed to the air [6].
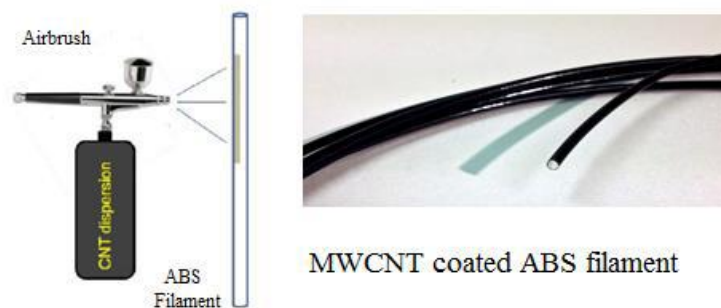

Figure 6: MWCNT coating on ABS filament.

In second step, we take advantage of the fact that CNTs display an extraordinary sensitivity to microwave exposure. Although the polymer filament is relatively insensitive to microwaves, the localized heating of the CNTs will cause selective melting at the filament-filament interface (Figure 7) and allow for polymer diffusion and formation of a continuous polymer structure that is markedly different than the native, as-printed 3D structure.
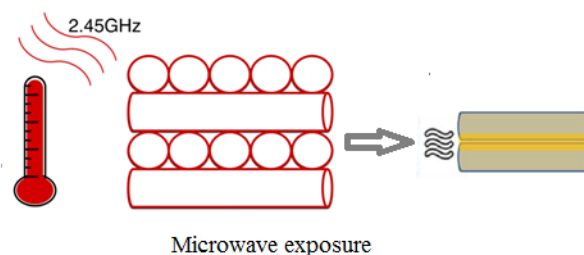

Figure 7: Microwave exposure of MWCNT coated ABS filament.

The final step, MWCNT coated acrylonitrile butadiene styrene (ABS) filaments are placed together to form a cross a crosshatch structure followed by ~20 seconds of exposure to microwaves in a conventional

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microwave oven in which microwaves will sinter the filament by reducing the air gap between intra adjacent filament in stage-1 and stage-2 as shown in figure 8. In Initial stage: Transport from high energy convex particle surfaces to concave surfaces, necks. Fusing, increased contact area. Pore volume and density remains almost constant (4-5% shrinkage, relative density 0.5-0.6), Intermediate stage: Interparticle neck growth, grain boundary area increase, interparticle grain boundary flattens, pore diameters decrease. (5-20% shrinkage, relative density up to 0.95), Final stage: isolated pores may remain at triple points or inside grain matrix. These pores may be gradually eliminated. (relative density > 0.95). This experiment demonstrates that the central concept of CNT-coatings for microwave-induced fusion is feasible [2].
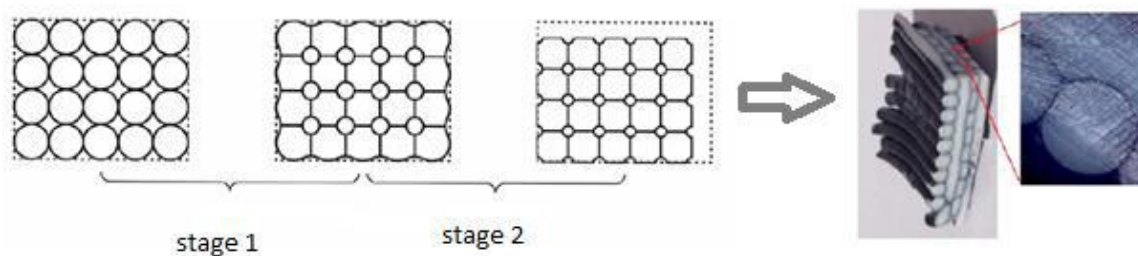

Figure 8: The filament fusion in two stages during sintering that occurs by microwave exposure to eliminate voids and improve load transfer.

4. FDM printing test specimens as per ASTM standards

The FAB X Pro hot bed 3d printer is used to print the test specimens as per ASTM standards, while 3d printing the test specimens the problem caused by only MWCNT coated ABS filament, the main challenge raised is nozzle clogging, this can be avoided by maintaining homogeneity in the filament coating to some extent. The 3 filaments, such as 1) MWCNT dispersed ABS filament, 2) ABS coated with MWCNT filament, and 3) Pure commercially available ABS filament are feeded to FDM 3D printer to fabricate the test specimens as shown in the Figure 9 [8,9].
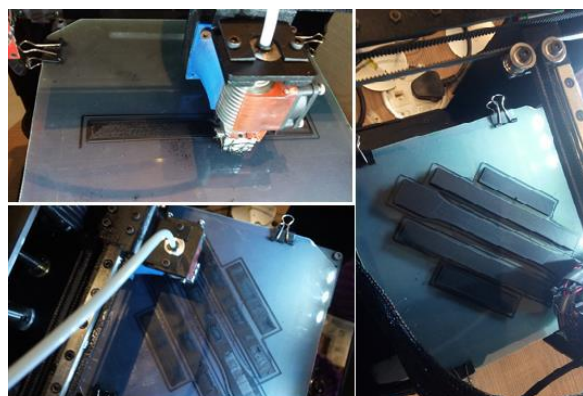

Figure 9: 3D printing of test specimens with 100% infill and 100 microns layer height.

5. Test Results

The effect of Multi Walled Carbon Nano Tubes (MWCNT) on ABS filament is presented in table 5.1. The influence of the MWCNT to change the bulk properties of ABS is studied by adding 15% of MWCNT to 80% of ABS resin along with 5% of proprietary adhesive for enhancing the material properties is provided in the table 1, column of MWCNT mixed ABS. The effect of MWCNT on surface properties of ABS is studied by coating MWCNT to the Pure ABS filament, the mechanical properties is presented in table 1 in column of MWCNT coated ABS.
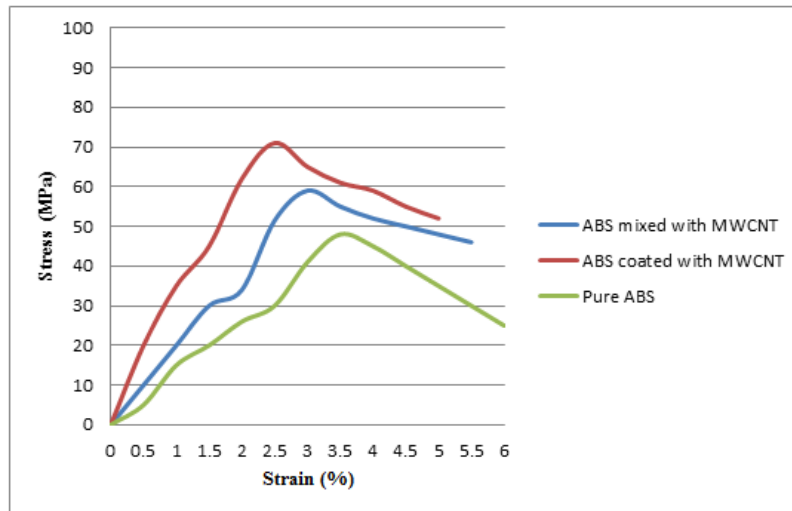
Table 1: Test results of average of 5 test specimens.

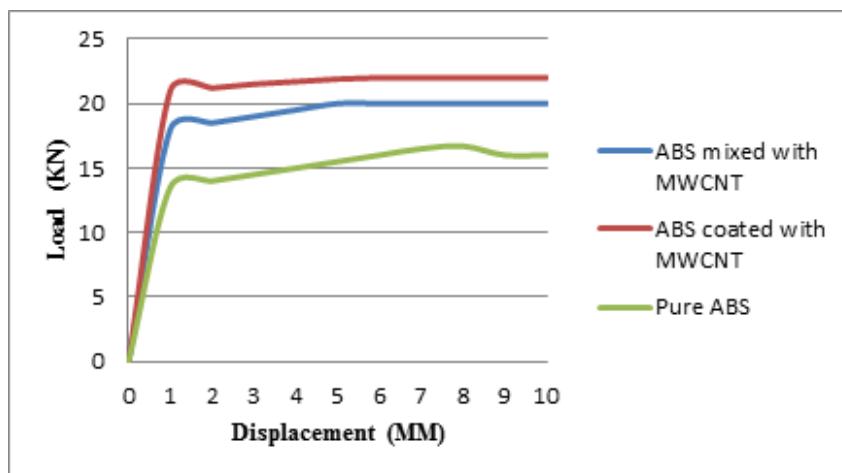| Property	Standard	Unit	MWCNT mixed ABS	MWCNT coated ABS	ABS
Tensile'Strength'(Yield)	ASTM'D638	MPa	51.5	62	41
Tensile'Modulus	ASTM'D638	MPa	2125	2350	1955
Tensile'Elongation	ASTM'D638	%	5.65	4.5	4.1
Flexural'Strength	ASTM'D790	MPa	80	89	68
Flexural'Modulus	ASTM'D790	MPa	2385	2182	1950
Izod'Impact, 'Notch	ASTM'D256	Ft-lb/in	9.5	12	3.75
Izod'Impact, 'NONotch	ASTM'D256	Ft-lb/in	18	21	9
HDT'(@66psi)	ASTM'D648	°C	125	113.5	97.5
Surface'Resistance	ASTM'D257	Ohms	105-107	107-109	>1013

5.1 Tensile Test Results

The coating of Multi Walled Carbon Nano Tubes (MWCNT) on pure ABS filament, increased the Tensile Strength by 51 % and by mixing the MWCNT in ABS the increase in tensile strength by 25.6% is observed. The considerable increase in tensile modulus of Pure ABS filament, MWCNT mixed with ABS and MWCNT coated ABS is observed respectively in table 1.

The percentage of tensile elongation is more in MWCNT mixed with ABS when compared to MWCNT coated ABS and pure ABS filament, the microscopically studying the influence of MWCNT on ABS reveals the increase in brittle ness of ABS by coating MWCNT on its surface is more when compared with MWCNT mixing with ABS but this has nearly similar percentage of elongation in comparison with pure ABS as per resultant data in table 1.

Graph 1: Stress (MPa) Vs Strain (%) of Pure ABS , ABS coated with MWCNT and ABS mixed with MWCNT.

The Graph 1 presents the variation of stress along with the percentage of strain of 3 filaments, they are Pure ABS filament, ABS coated with MWCNT filament and ABS mixed with MWCNT filament.

Graph 2: Load (KN) Vs Displacement (MM) of Pure ABS, ABS coated with MWCNT and ABS mixed with MWCNT.

The Graph 2 provides response of 3 filaments to increase load in KN. The load bearing capacity is increased in pure ABS filament, ABS mixed with MWCNT, ABS coated with MWCNT respectively.
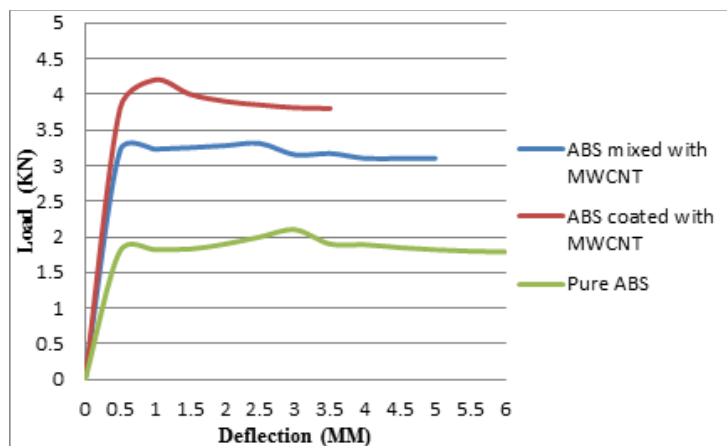
The coating of MWCNT to pure ABS filament and exposure to microwaves in post processing will increase the intra layer bonding with in the 3d printed part. The FDM 3d printed parts has intra layer gap in micro scale, this leads to failure of the 3d printed part when loaded externally, to decrease this

failure and increase the load bearing capacity of 3d printed parts, they should be fabricated by MWCNT coated filaments and post processing it by exposing to microwaves will decrease the intra layer micro scale gap drastically, this is observed physically in shrinking of the 3d printed part after post processing with microwaves.

5.2 Three point bend Test Results

The three point bending test is performed on the pure ABS filament, ABS mixed with MWCNT and ABS coated with MWCNT, The increase in 30% of flexural strength by coating MWCNT to ABS filament is observed and the increase in 17% of flexural strength by mixing MWCNT to ABS is obtained as per the result obtained per performing the Thee point bend test as per ASTM D790 standards presented in the table 1.

The considerable increase in the flexural modules of pure ABS filament, ABS coated with MWCNT and ABS mixed with MWCNT are 1950 MPa, 2182 MPa and 2385 MPa respectively by three point bend test results obtained as per ASTM D790 standards.

Graph 3: Load (KN) Vs Deflection (MM) of Pure ABS, ABS coated with MWCNT and ABS mixed with MWCNT.

6. Current Work

This work has shown that it is currently possible to synthesize MWCNT/ABS nano-composite materials that are compatible with commercial off-the-shelf 3D printers. This work has shown that nano-composite materials have functionality in a 3D printer and that even in ultra-high concentrations can be made into viable composites. 51 % increase in tensile strength by coating MWCNT to pure ABS filament and 25.6% increase in tensile strength by mixing MWCNT to ABS is observed. The increase in 30% of flexural strength by coating MWCNT to ABS filament is observed and the increase in 17% of flexural strength by mixing MWCNT to ABS as per the result obtained by performing the three point bend test. The study of this filaments microscopically reveals the increase is the strength is in contrast of increase in the brittleness of the filament is due to the propitiatory adhesive agent which is the herbal extract. There is a drastic decrease in the surface resistance is observed by adding or coating of MWCNT to ABS filament, this opens avenues to the vast application of this filaments in electronic applications.

7. Future Scope

Additive manufacturing is a multi-disciplinary field that encompasses many aspects of chemistry, physics, and engineering in a manner not so dissimilar from its nanoscale counterpart, in the field of nanotechnology. The two areas of development that steer advances are the composition of the next generation of filaments, pellets, and resins for 3D printing; and the equipment used for filament production.

As per our detailed study on usage of nano materials in additive manufacturing, there is a high scope of using nanomaterials in all the seven Additive Manufacturing (AM) processes like material extrusion, Vat photo polymerization, material jetting, binder jetting, powder bed fusion, sheet lamination, direct energy deposition. Nano materials can be used in various forms in different 3d printing techniques such as Nanomaterials mixing in binder ink for good bonding process which possess less viscosity and density, Nano materials coating on papers in sheet lamination process and coating on 3d printer filaments for more part strength. Nanomaterials in amorphous form is mixed with powder in power bed fusion processes for grain bonding and strength enhancement. Nano metallic materials in direct energy deposition process will increase the strength of the 3d printer parts. Nanomaterials mixing with resins to increase the load bearing capacity of Vat polymerized process printed parts.

The principal area that future work as per observation of drastic reduction in resistance of the ABS by adding CNT, will helps to investigate the utilization of CNT excellent electrical conductivity and the possibility of the use of CNT nano-composites in creating electrically conductive 3D printed parts. This could be highly beneficial to many areas principally any area that needs a rapid prototyped part that must be conductive which could allow for both the possibility of 3D printed circuit boards as well as electro static discharge (ESD) compatible 3D printer material. This work would seek to determine if an electrically conductive 3D print material can be synthesized and allow for the rapid prototype of electrically conductive material in commercial off-the-shelf 3D printers.

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