FACULTY OF CHEMICAL AND MATERIALS TECHNOLOGY
DEPARTMENT OF POLYMER MATERIALS

"THE EFFECT OF SONOCHEMICAL PRE-TREATMENT ON DISPERSION QUALITY OF CARBON NANOTUBE IN NYLON 66"

Master's thesis

Yashwanth Swamygowda

Supervisor: Tiia-Maaja Süld

Specialist

Co-supervisor: Pasi Keinänen

Researcher

Technology of Wood and Plastic, KVEM 12/13

Tallinn 2016

TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

KEEMIA- JA MATERJALITEHNOLOOGIA TEADUSKOND
POLÜMEERMATERJALIDE INSTITUUT

“SONOKEEMILISE EELTÖÖTLUSE EFFEKT SÜSINIKNANOTORUDE DISPERSIOONI OMADUSTELE NAILON 66-S”

Magistritöö

Yashwanth Swamygowda

Juhendaja: Tiia-Maaja Süld

Spetsialist

Kaasjuhendaja: Pasi Keinänen

Teadlane

Technology of Wood and Plastic, KVEM 12/13

Tallinn 2016

Declaration

Hereby I declare that this master's thesis, my original investigation and achievement, submitted for the master degree at Tallinn University of Technology has not been previously submitted for any degree or examination.

All the work of other authors, important aspects from literature and data from elsewhere used in this thesis are cited or (in case of unpublished works) authorship is shown on the text.

Yashwanth Swamygowda

MASTER’S THESIS ASSIGNMENT

Student data:

Name of the student: Yashwanth Swamygowda Student code: 132102 KVEM

Signature:

Master´s thesis topic:

“The effect of sonochemical pretreatment on dispersion quality of carbon nanotube in nylon 66”

“Sonokeemilise eeltöötluse effekt süsiniknanotorude dispersiooni omadustele nailon 66-s”

Supervisor: Tiia-Maaja Süld

Signature:

Employment: Tallinn University of Technology, Department of Polymeric Materials, Chemical and Materials Technology

Profession: Specialist

Co-supervisor: Pasi Keinänen

Employment: Tampere University of Technology, Department of Material science.

Profession: Researcher

Aim and tasks of the master´s thesis:

The aim of the thesis is to study the effect of sono-chemical pretreatment on carbon nanotubes, its dispersion quality and develop the suitable method to incorporate carbon nano-tubes in nylon 66 polymer for better applications.

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

ASTM	American society for testing and materials
ATR	Attenuated total reflection
^{o}C	Celsius degree
Cp	Heat capacity at constant pressure
CNT	Carbon nanotube
CVD	Chemical vapor deposition
DWNT	Double walled carbon nanotube
FPV	Filter pressure value
FTIR	Fourier transform infrared spectroscopy
HSSM	High Speed Shear Mixer
IUPAC	International union of pure and applied Chemistry
J	Joule
KBr	Potassium bromide
L/D	Length/ Diameter
MSDS	Material safety data sheet
Pas	Pascal
RPM	Rotation per minute
Sample ‘A’	Virgin nylon 66
Sample ‘B’	Nylon 66 passed in Extruder
Sample ‘C’	Nylon 66 with pristine CNT in extruder

Sample ‘D’	Nylon 66 with water sonicated CNT in extruder
Sample ‘E’	Nylon 66 with pristine CNT in compounder
Sample ‘F’	Nylon 66 with water sonicated CNT in compounder
SEM	Scanning electron microscopy
SWNT	Single walled carbon nanotube
TEM	Transmission electron microscopy
TGA	Thermo gravimetric analysis
T_g	Glass transition
Tm^1	First melting point
Tm^2	Secondary melting point
TSE	Twin screw extrusion
UTM	Universal testing machine
ϕ	Diameter
ϵ	Energy density
eV	Electron volt
γ	Fluid rate
σ_s	Shear stress
η	Viscosity

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Taking an account of many recent researches from polymer composite materials and its applications in structural engineering sector shows very rapid growth. Metallic materials gradually replacing and loosing there places due to introduction of engineering and super specialty polymers. Polymers, which can replace those easily with an advantage of its less weight in ratio by without compromising in any other properties of metals. Young and new generation is heading towards more advanced methods to build a remarkable history in the depth of nano scale. Examples like clay, graphite, silica and carbon nanotubes (CNTs) are widely using. Among that CNTs like material as fillers in polymers opened various applications in the field of aerospace, marine, defense and automotive industries dude to its very low aspect ratio and high strong in strength.

Considering the vast market for polymers nowadays in automobile sector still many parts are not replaced by polymers even though have a slight changes to fix it. Safety has considered a most important factor in vehicles manufacturer understanding, the metal replacement adjustments are made them up scary. Example since the polymer gears are capable to use and execute in market few of their drawbacks are not letting them to enter completely. Few reasons like replacement after some ‘n’ number of cycles, heat dissipating capacity, chemical resistivity, thermal characteristics, and high temperature tolerance effect and so on. Even though many techniques are currently available to synthesis, still we are lacking to find the suitable for CNTs dispersion.

To overcome with these kinds of challenges, using the knowledge on CNTs history and its applications broadly, I have setup up my mind to study and develop a smarter method in “ the effect of sonochemical pre-treatment on dispersion quality of carbon nanotube in nylon 66”.Secondly I also considered to aim towards increase its mechanical, electrical and physical properties.

1.1 Carbon nanotube

Since the carbon nanotubes belong to fullerene structural family. They are obtained by rolling up of graphene sheets. The graphene sheets are rolled at special and different angles which result in different properties for CNTs. CNT enjoys long and hollow carbon structure with unique properties such as thermal and electrical conductivity, semiconducting behavior and good mechanical properties.

As mentioned, the graphene sheets are rolled up with special angles which lead to form different kind of CNTs including chiral, zigzag and armchair is shown in Figure 1. In the Figure 1, “n” and “m” describe how the graphene sheet is rolled up for forming the nanotube; “T” presents the tube axis, also “a1” and “a2” are the unit vectors of graphene in real space.

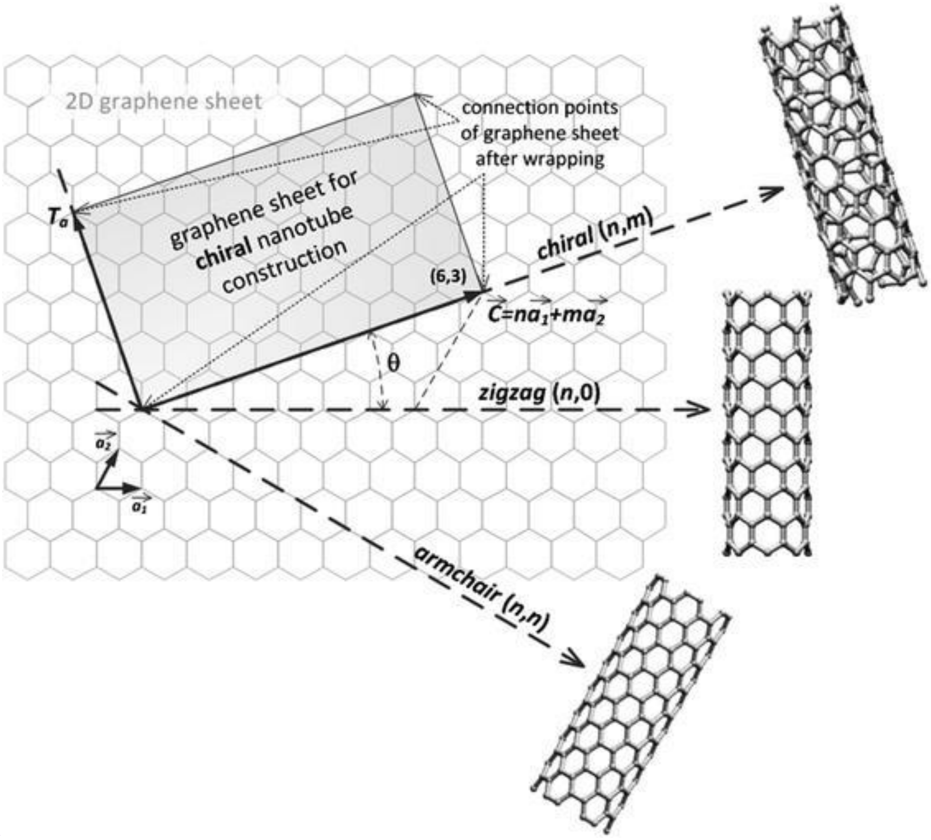


Figure 1. Graphene sheet and rolling up to form CNTs.[1]

For first time in 1856 scientist Brody started the preparation of CNTs by using graphite and sulphuric acid material with oxidizing agents as potassium permanganate. Soon after in 1896, Hummer prepared by nitric acid and sulphuric acid mixtures. Carbon nanotubes were observed by Radushkevich and Lukyanovich in 1952[2]. Many scientific papers have cited that single wall CNTs were observed in 1976 by Oberlin [3] . Later the multiwall carbon nanotubes (MWNTs) are discovered by Sumio Iijima in 1991 using arc discharge growth method1[4]. Basic classification of CNTs are based on the number of the layer categorizes. CNTs including single walled carbon nanotubes (SWNTs), double walled carbon nanotubes and MWNTs, which are shown in Figure 2. CNTs are formed by undergoing SP^2 hybridization of layers of graphite sheets made up of single carbon atom thickness [5].

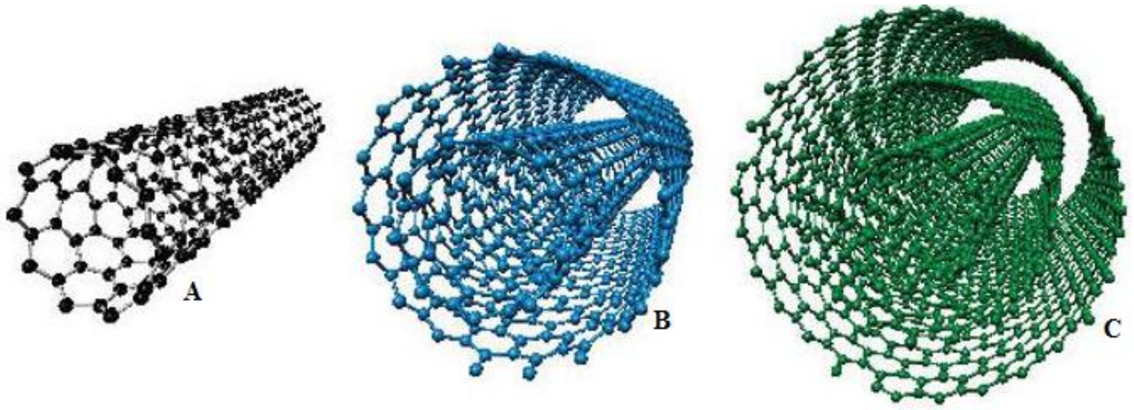


Figure 2. (A) Single wall carbon nanotubes (SWNTs), (B) Double wall carbon nanotubes (DWNTs) and (C) Multi wall carbon nanotubes (MWNTs).[6]

Now-a-day's CNTs are taken as an extremely in consideration due to its low density, strong, stiff and tough which is almost one sixth weight and strong strength about 30 to 100 times compare to steel is highly remarkable. Using CNTs as a fillers trying to develop an immeasurable applications in the field of polymers. Polymer composite areas are consuming more fillers today to enhance mechanical properties, surface property, electrical conductivity and thermal conductivity, also cell membrane and drug delivery systems in pharmaceutical applications are seeking a new approach towards innovation using CNTs [7].

CNTs are synthesized using more several methods. Namely chemical vapor deposition, Arc-discharge, laser ablation, flame pyrolysis, flame synthesis, high-pressure CO disproportionation, pyrolysis or vapor-phase deposition, vapor-phase growth, electrolysis, hydrothermal, sonochemical and so on. Among these methods the more economical and conventional methods are shown in Figure 3.

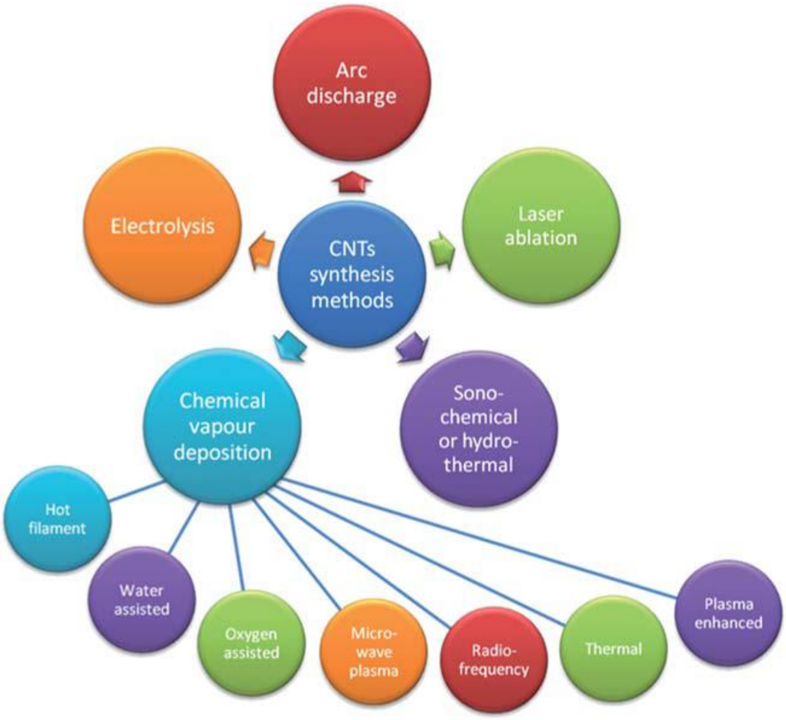


Figure 3. Major CNTs synthesis methods.[8]

Chemical vapor deposition (CVD) is common method for producing CNTs. In the CVD process, volatile molecules are carried out in the vapor phase and then are transported to a heated substrate. In this part, heterogeneous reactions happen for depositing of product. Figure 4 presents schematically CVD process [9].

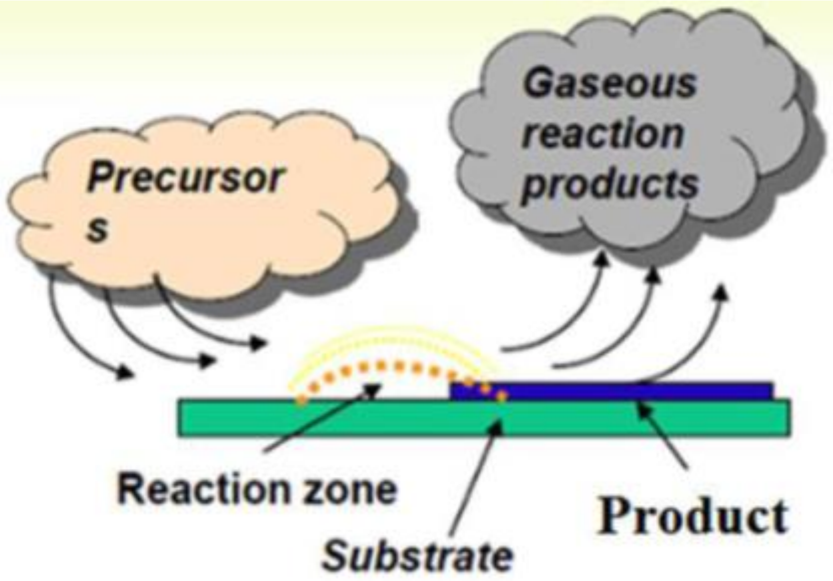


Figure 4. Chemical Vapor deposition (CVD) method.[9]

Figure 5 shows the CVD method for producing CNTs, using carbon source in the gas phase (methane, carbon monoxide and acetylene) reaction in the furnace at temperature 600 to 900 ˚C. In continue, CNTs product is deposited on the substrate which is coated by catalyst (usually metals such as Ni, Fe or Co) [4, 7]. The diameter of CNT particles is related to CVD experimental parameters (Figure 6) [6].

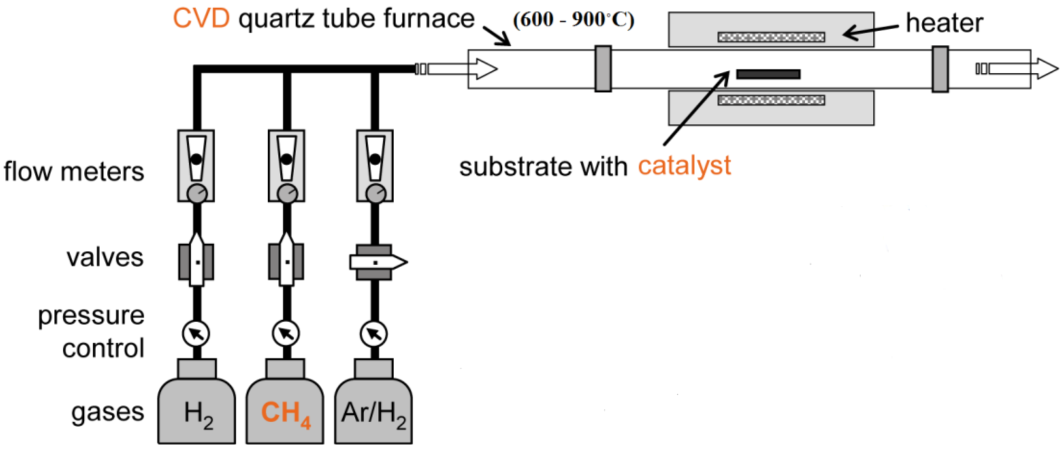


Figure 5. The CVD reaction for synthesis of CNTs.[10]

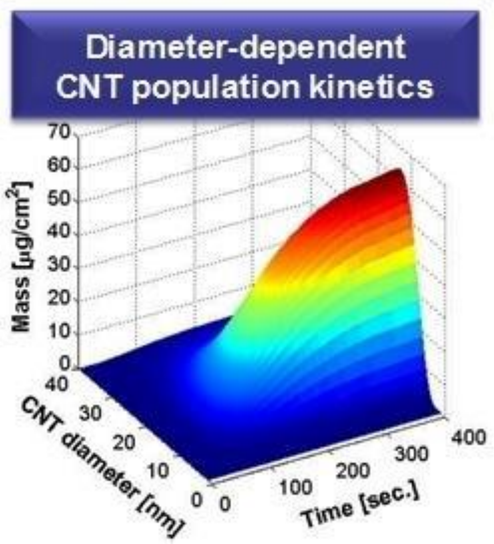


Figure 6. Relationship between CNT particles size and CVD reaction rate. [11]

Amount of yield for this method is 30 to 90%. The other advantages of this method are like ease in producing purer, SWNT and MWNT with few structural defects, possibility for open air synthesis and being chip can be mentioned[12].

Peculiar aspect ratio in structural property of CNTs are advantageous. As fiber reinforcement they increase the interfacial surface between fibers and matrix improving the quality of adhesion. Improve in adhesion leads to higher absorption during crack propagation, which increases the interfacial strength of the laminate in a structural composite material [13]. It’s not an easy task as we think to prepare or develop a new products using CNTs. The biggest challenge and truth is not openly available to all unless in-depth of needed to use and handle it as like a normal fillers. Due to strong Van Der Waals forces between CNTs leads to re-aggregation and formation of agglomerates. This remains as a change in dispersion of CNTs in polymer matrix. To find solution for this problem are noted below. Because of this hard nature in behavior has taken into serious minds to find solutions in various methods. To develop high performance polymer nonocomposites with MWNTs certain key factors should be noted [14].

a) Functionalization of CNTs.
b) Equal distribution and dispersion of CNTs in polymer matrix.
c) Structural properties of CNTs inside the polymer matrix
d) Suitable methodology and contractibility during polymer synthesis with CNTs.

Considering the above factors, dispersion as a main key factor in CNTs to uniform distribution inside the Polymers should be developed and optimized. Dispersion factors are also depends on the solvent used for functionalizing the CNTs. This should be enough functional groups to bind with polymer matrix material while synthesizing. Some of the polymers like polydimethylsiloxane (PDMS) are cable to intake 9% of its weight MWNTs through strong chloroform organic solvent. Through many reviews we have noticed some of the solvents are also able to possess same behaviors like chloroforms as an example stated before. It taken to find the proper solvent again. By keen observation from previous research considering solubility and density factor which should be close enough to matrix are elected to conduct our experiment [15].

1.2 Sonochemical treatment

Sonochemical is a method which measures the effect and activities of chemical solutions when treated with ultrasonic waves. In simple wards, a process to bombard the particles and activate using sound energy. It also functionalizes the nanoparticles and helps to disperse in liquid phase by creating tiny cavities on it. Fine particle milling, dispersing, homogenization and emulsification so on are the main application of this technique. Robert Williams observed this behavior first time. Using nitric and sulphuric acid CNTs are modified and attaching functional groups by decomposition of organo metallic nano particles on their surfaces[16]. Sonication energy is directly proportional to the dispersion concentration of CNTs in polymer. Sodium dodecyl benzene sulfonate as shown this property. CNTs functionalized having oxygen groups and low sonication energies compared to other relative groups [17].

Sonochemical pretreatment has involved major importance to activate CNTs. CNTs bundles are beak down using optimal energy and power. Process should not exceed the condition or else this leads to shorting of tubes and damage the structure. By this conductivity get decreases. Considering all factors, a mild sonication bath would be an ideal option as it allowed high quality of dispersion yet avoided severe damaging of CNTs during sonication [15].

CNTs with higher outer diameter had strong Van Der Waal forces. Solvent used for sonication should have proper compatibility with CNTs. Many acids are avoided because of hazardable and non-environmental friendly process. Water found as a neutral and nature friendly in this case. Considering water as a solvent, many procedures are developed. But its high Van Der Wall forces forms agglomeration between CNT and water solubility reaction. Covalent and non-covalent techniques can alter the aspect ratio of CNTs. This varies the dispersion results. Techniques like covalent and non-covalent are designed to overcome with above problem. In covalent functionalization, carboxyl functional groups are generated by oxidation reaction and grafted. Grafting impacts on low electrical, mechanical and optical properties. In non-covalent functionalization, usage of dispersing agents like surfactants and organic solvents helps to dispersion [17]. It is evident the quality of dispersion and distribution inside the matrix material. Taking investment and processing cost in to account in industrial scale setup, it’s a bit lengthy procedure to handle these many step and finally it reflects at the end product. Therefore by preventing all the above existing process looked towards mechanical way to find solution through this work.

1.3 Polymer matrix selection

After the invention of polyamide polymer in 1935 by Wallace Carothers at DuPont’s research facility in ‘The United States of America’ it was called as first commercially successful synthetic thermoplastic in polymers. Polyamides are prepared by melt poly condensation process. Hexamethylene diamine and adipic acids are used as monomers. In aliphatic polyamides, nylon 66 plastics are formed from adipic acid and hexamethylene diamine. It is highly distinguished due its good resistance to acids, tensile strength, abrasion resistance and toughness at high temperature service condition even though its having low glass transition temperature (T_g) compared to other polymers [18].

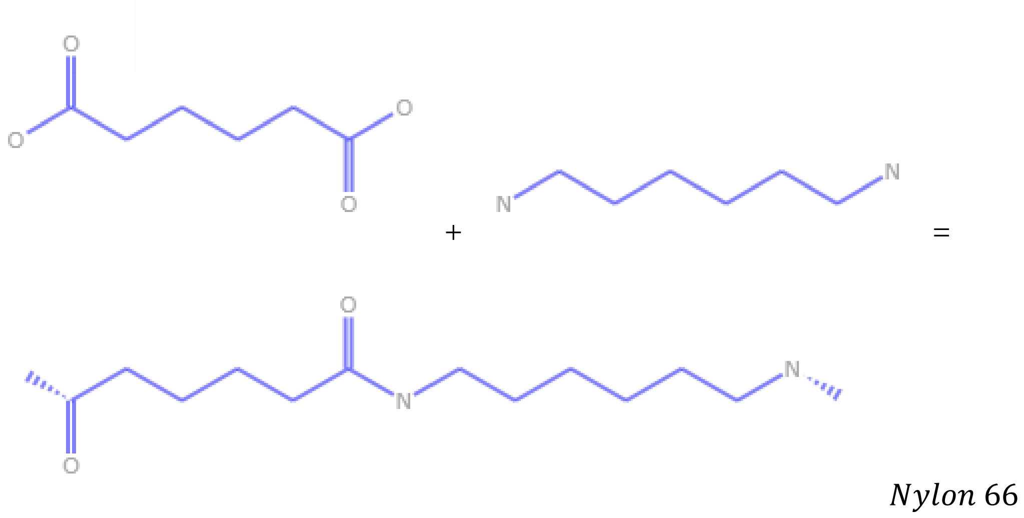


Figure 7. Adipic acid with hexamethylene diamine reaction forms nylon 66 structure.[19]

Considering nylon 66 non-solvent property to acids, alkalis, aromatic and chlorinated solvents, standard hydrocarbons, chloroform, alcohols, ether, ketones and esters, made us to choose as a matrix material. Except solvents like m-cresol, chlorophenol, formic acid, acetic acid, phosphoric acid [20]. Resistance characteristics too many common solvents are taken into an important factor in our work due to future application development concept if any possible chance to get continue this work. In that soluble solvents formic acid is the only one which an easily dissolve nylon in it. External forcing aid like temperature and pressure to dissolve also be avoided. For dissolution purpose of nylon by floating in formic acid advanced by close density parameters between one another [15]. Nylon 66 is conditioned at lab under dehumidifier for 24 hour to prevent moisture before taken to further processing actions.

1.4 Solvent selection

According to systematically named from IUPAC a solvent called methanoic acid is choosed. Generally also noted by other names are named as formic acid, aminic acid, hydrogen carboxylic acid, , hydroxymethanone, hydroxy-oxo-methane, metacarbonoic acid, oxocarbinic acid, and oxomethanol.

Formic acid is found as good solvent to the Nylon 66 polymer. So matrix material can easy soluble in the chosen solvent. Also it can be easily removed from drying process.

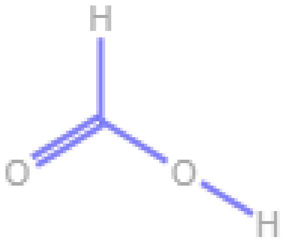


Figure 8. Formic acid structure.[21]

2. AIM OF THE RESEARCH

The aim of the thesis is to fulfil the following objectives:

a) To study effect of sonication or sonochemical pre-treatment on CNTs.
b) To study the involvement of twin screw extrusion and compounder processing techniques and its effects on dispersion quality.
c) To study the incorporation of CNTs filler effects on its mechanical properties.

3. EXPERIMENTAL METHODS AND TECHNIQUES

3.1 Materials

In this work polymer nylon 66, a semi crystalline material purchased from a Swiss manufacturer EMG-CHEMIE AG group of production plant. Purchased nylon 66 grade type belongs to Grilon AS/2 type, an unreinforced polyamide injection molding grade. Good flow behavior, easy processing, and shot cycle time are important properties to make this choice. According to the material data sheet supply, general properties like density of 1.14 g/cm^3 and moisture absorption of 2% at 23^{o}C/50% rh. Nylon 66 was kept in desiccant dryer for 8-10 hour at 80^{o}C before taken in to further experimental levels.

As a filler, carbon nanotubes (CNTs) were imported from Belgium manufacturer NANOCYL S.A, grade NC7000 multi-wall carbon nanotubes (MWCNTs) used throughout our research. It’s average diameter in 9.5 nanometers, average length in 1.5 microns both are confirmed through transmission electron microscope (TEM) method of measurement. 95% of Purity and 10% of metal oxide content confirmed from thermo gravimetric analysis (TGA).Through brunauer-emmett-teller (BET) surface area of 250-300 m^2/g data were gathered.

A suitable solvent formic acid purchased from Fisher chemical industries. Consist of molar mass 46.03 g.mol-1, density 1.22 g/cm3, melting and boiling point of 8.4oC and 100.8oC. Nylon 66 polymer matrix is slowly added to the solvent by stirring with the help the help of magnetic stirrer until it get saturated clear solvent. Found that 200g of nylon 66 can dissolved in 466g of formic acid and until saturation point. Total weight of 666g per batch is prepared each time.

3.2 Sonication method

We choose a flexible device from the manufacturer ‘Hielscher’, a model UIP-1000hd makes ease in very adaptable use. The figure is shown below. Theoretically by considering the specification of sonicator it exhibits 20 kHz, and 1000W. But in practice from the estimation of different result basis noted as one fifth of its power only utilized to activate our particle.

A small quantity 0.2 – 0.3g of CNTs added in to 450-470 ml distilled water and stirred well manually. Then the mixture is taken to sonication chamber and immersed inside the connector. Left for optimized time around 20 min to activate the carbon nano particles inside water under sonication process. Due to exothermic reaction, heat is developed and allowed to cool naturally in lab condition. Using filter paper CNTs separated out from water and taken to dryer for 24 hours at 110°C to ensure that water particles will not to affect the nylon 66 properties before and after compounding.

Figure 9. Hielscher make sonicator.[22]

After drying, CNTs were observed inside a beaker like a group of clusters or agglomerates due to highly attractive Van Der Waals forces between the molecules. To get back to the dry and individual clear form structure crushing process was adopted. Using pestle and mortar, manually it’s handled and separated. Then CNTs were directly taken to a mix with the polymer matrix for direct extrusion process and to disperse in high speed mixer it was crushed and made a fine particle to easy the dispersion and distribution during the further processing level in compounder.

3.3 Solubility test

Solubility is an important factor when it considers to miscible and immiscible things raised. So the compatibility has to achieve between matrix, solvent and filler. The prepared solvent mixture will introduced to high speed mixture to formulate a master batch. Later processed using twin screw extruder and compounder[23].

According to MYR manufacturer, VR rotational ‘V1’ type, Model ‘L’ viscometer offer viscosity measurements as per the ISO 2555 standard was conducted the experiment and recorded the values from rotational viscometer [24]. A small quality of approx. 50 gm is taken for solubility test to get viscosity and shear stress of the solvent. Viscosity of 73205Mpas and 100Mpas is directly recorded and noted.

Figure 10. Rotational viscometer.[25]

Depend on the obtained shear stress value, it is placed in high speed shear mixer equations to find the angular velocity of the blade. Through this, it is able to set the motor blade rpm to disperse nano particles inside the polymer solvent mixture.

3.4 High speed shear mixing method

In general mixing can be done by transferring the mechanical energy to media to discrete the mass. Mass has strongly holed by the binding energy between the masses. Considering these two important factors like mass and binding energy, more effective technique is needed to separate the mixtures. On this case our CNTs aggregates binding energy should be less than the applying energy from the chosen high speed shear mixing equipment. Then only the separation of particle can be achieved. From the another prospect to keep the individual CNTs morphology same as original even though after treating with sonication, the applied energy in used technique should reach only between aggregated binding energy and individual CNTs which are resisted toward its own fractures from the other external energies. If we maintain this ideology to process the aggregated CNTs then we can see the wetting and separation of particles from the media. To minimize the strain energy, MWNTs the length should be closed orders in to single packs. Where contacts can be packed closely and bind closely with increase in nanotubes length. Because of this close structure it gets a cross linked chains structure and physical become very strong. But in practice we can show this developed contact energy in terms of energy density (ϵ). In the below equation (1) shows the energy density required to separate MWNTs [26].

$$\epsilon \sim C_t |V_{tot}| \tag{1}$$

Looking electron micrographic image and estimated, C_t at the spacing junction $\zeta \sim 100$ nm approximately between the neighbouring nanotubes visible on the surface of a cluster, it can be written as equation (2) below.

$$C_t \sim {}^{1}\!/_{\zeta^3} \tag{2}$$

$$V_\perp \sim -100\, eV \text{ for } \phi\, 60 - 100 \text{ mm}$$

$$\text{Then } \therefore \epsilon \sim 16 \text{ kPa (energy density)}$$

The above result shows the minimum energy required to separate each MWNTs bundle also called as activation energy. By this, the minimum resulted activation energy must need to beak the binding energy between the CNTs in practice. Therefore using the above data, by substituting in shear stress (σ_s) (100 Mpa obtained from rotational viscometer), defined by the product of viscosity (η) (73205 Mpas also obtained from rotational viscometer) and fluid rate (γ) is narrated below as equation (3).

$$\sigma_s = \eta\gamma \tag{3}$$

For a high speed shear mixer and extrusion both are carried out in low viscous solvent media by dissolving matrix polymer nylon 66 in formic acid. From the literature for this condition η in high speed shear mixer will in between 0.01 to10 Pas. Calculating the fluid rate, equation (4) and substituting in above equation (3) provides the angular velocity. This means the minimum speed to set the motor to achieve the least dispersion quality in shear mixer is determined below.

$$\gamma = {}^{RW}/_{h} \tag{4}$$

where
R - radius of blade, m
W - mixer blade speed, rad/s (angular velocity)
h - space between mixer blade and inner walls, m

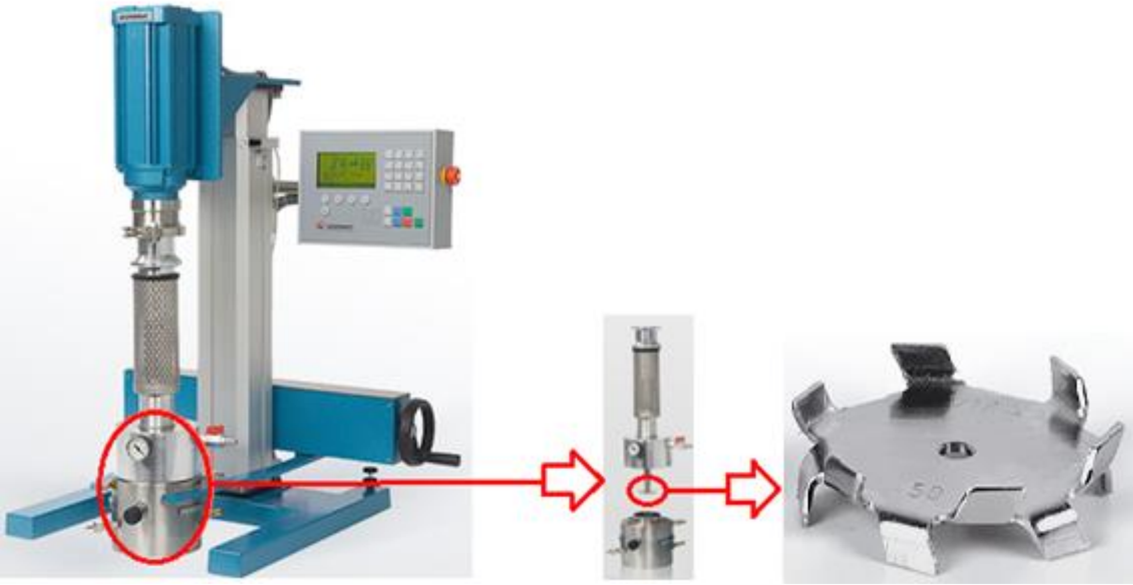


Figure 11. High speed shear mixer machine and the blade used for the experiment.[27]

High speed shear mixer or dispermat machine functionalizing blade radius 0.0258m and space between mixer blade and inner wall 0.01429m was calculated using slide caliper. Dispermat blades are geometrically designed to disperse, homogenize, stir and mixing functional capability. By calculating the angular velocity from the above equation which is approx. min 756.6 rpm to set in shear mix, we have adjusted that minimum value by raising it to 1000 rpm.

After adjusting the blade speed for dispersion, to run the experiment the sample size should fill minimum of 90% level. So that blade will in center of the pot and particle should disperse equally inside the mixture. To fill 90% of the sample holder pot, 316g of polymer solvent mixture is taken and started the experiment. Initially by adding 1g sonicated CNT and consequently after 5 and 10 minutes 0.5g of total 2g of CNTs are allowed inside the dispermat machine. Every 5 minutes temperature of the mixture is noted. On 35th minute, temperature was noticed from initial 5th minute 30°C to 46.2°C. At 40th minute temperature started to rise in high rate from 48.6 °C and above. Because of this limitation dispermat is equalized to 40 minutes. After dispermat process 30% weight in ration of 95.8g nylon 66 and 2% weight in ratio of 1.99g sonicated CNT's and remaining of formic acid, in total of 318g of prepared sample were taken to dryer at 110°C for 48 hr. Drying was to evaporate formic acid and moisture content.

The conceptual work process inside the dispermat machine is illustrated using below figure.

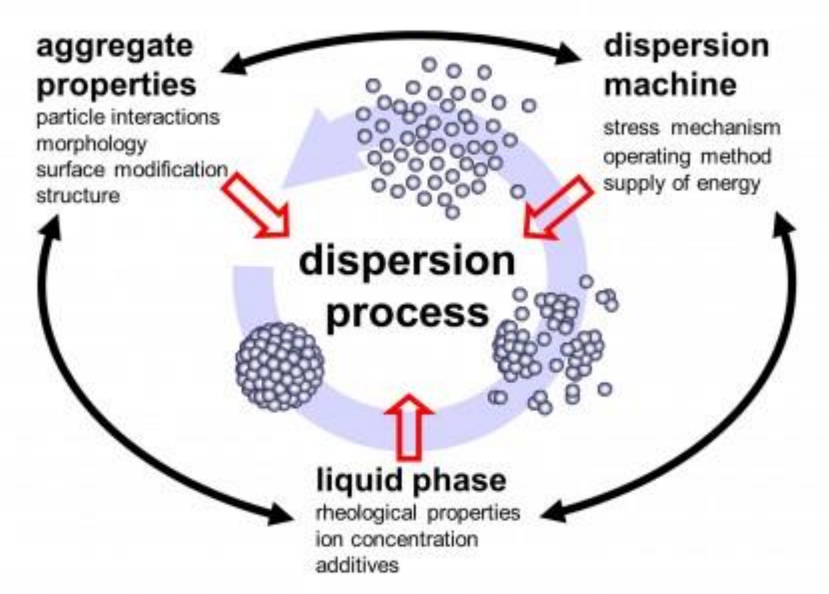


Figure 12. Nanoparticles dispersion process.[28]

After dying 30%weight prepared master batch added with 70% weight in ratio to virgin nylon 66 polymer matric. Mixed in tumbler mixer and taken to extrusion and compounder to study the effect of processing techniques on prepared master batch sample.

3.5 Extrusion processing technique

Extrusion is a process of mixing or compound of different compactable material with the external force and temperature. Mainly used for cross sectional products to form a specific shape modules. Brabender DSC25 Extruder is used to perform our test. It consist of nine barrels, vacuum pump, gravimetric feeders and two hole circular die is used. Barrel temperature from feeding zone to die are maintained between 250 to 265 °C. Machine specification, notification and other important details are shown below.

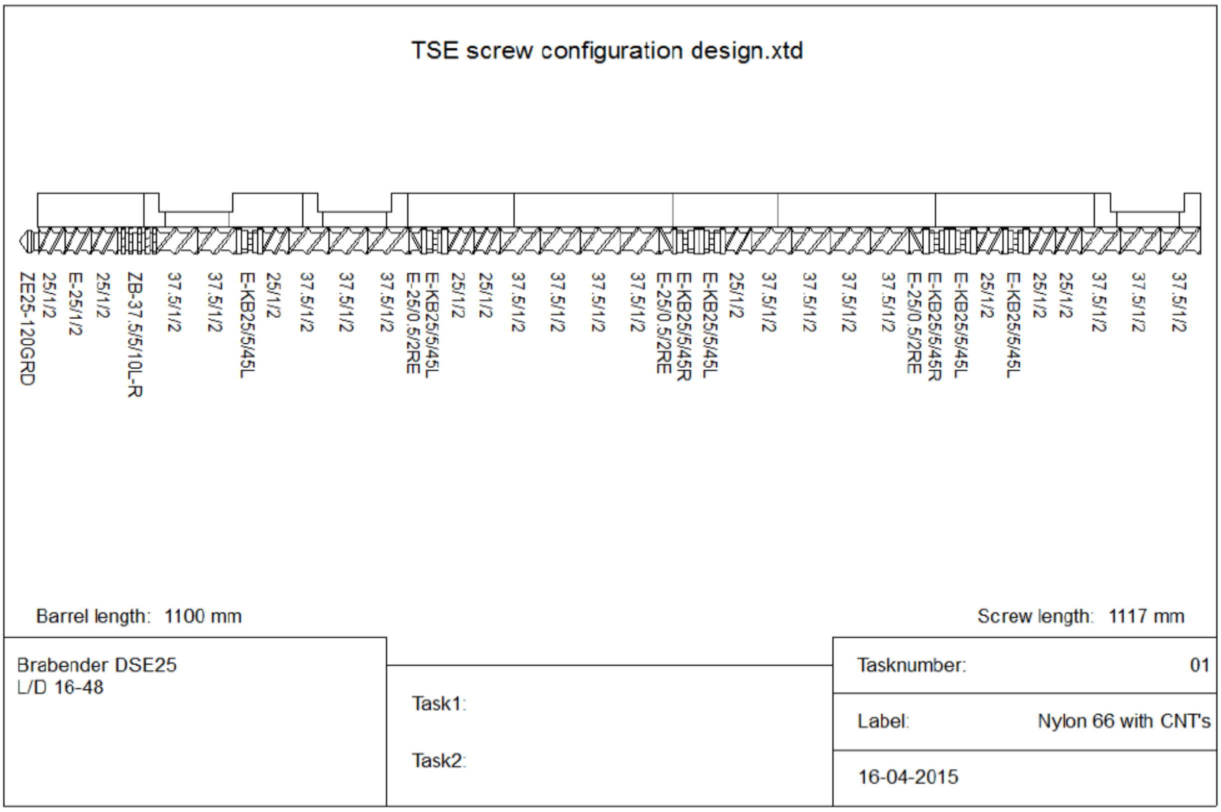
Table 1. Sample name and its notification.

Sample Notification	
Sample A	Virgin nylon 66
Sample B	Nylon 66 passed in extruder
Sample C	Nylon 66 with pristine CNTs in extruder
Sample D	Nylon 66 with water sonicated CNTs in extruder
Sample E	Nylon 66 with pristine CNTs in compounder
Sample F	Nylon 66 with water sonicated CNTs in compounder

Table 2. Extruder machine specification

Brabender DSE 25 TSE	
Screw Dia	25 mm
L:D ratio	16-48
Maximum torque	3151 /mm
Screw momentum	2x90 Nm
Maximum temperature	400 °C
Maximum melt pressure	30 MPa
Output	0.6 - 50 kg/hr

Figure 13. Brabender DSC25 extruder.[29]


TSE screw configuration design.xtd

Barrel length: 1100 mm

Screw length: 1117 mm

Brabender DSE25
L/D 16-48

Task1:

Task2:

Tasknumber: 01

Label: Nylon 66 with CNT's

16-04-2015

Figure 14. Screw deign used inside the brabender DSE 25 extruder.

The above screw designed is used due to limited number of elements and its availability. Screw elements effects also majors the results. Such as the elements like kneading blocks, mixing elements and other special dispersing elements (fractional mixing) are very important to get good impressive results.[30]

In clear, sample ‘B’, ‘C’ and ‘D’ are prepared using extrusion process in our research.

3.6 Compounder processing technique

Compounder is used to make clear distributive mixing in our experiment. It ensures the qualitative mixing and dispersive clearance for some extent with the use of twin screw technology in it. Mixing is done between three zone temperature set up 270, 280 and 285 °C at 250 screw speed rpm. The biggest advantage by using this machine is that, the melted polymer can be circulated inside the mould for many number of cycles if the quality of sample is not good enough. In our studies it taken to be a one minute for circulation once the intake is completely filled and packed tightly. This we can optimized later depending on quality of output. Because considering the change in melt cycle may changes the result vice-verse. Then the molten polymer is directly transferred to hand mould transfer by manually. Injection moulding machine is set for lab optimized condition to prepare a specimens for testing and further studies.

In clear, samples ‘E’ and ‘F’ are processed using compounder in our research.

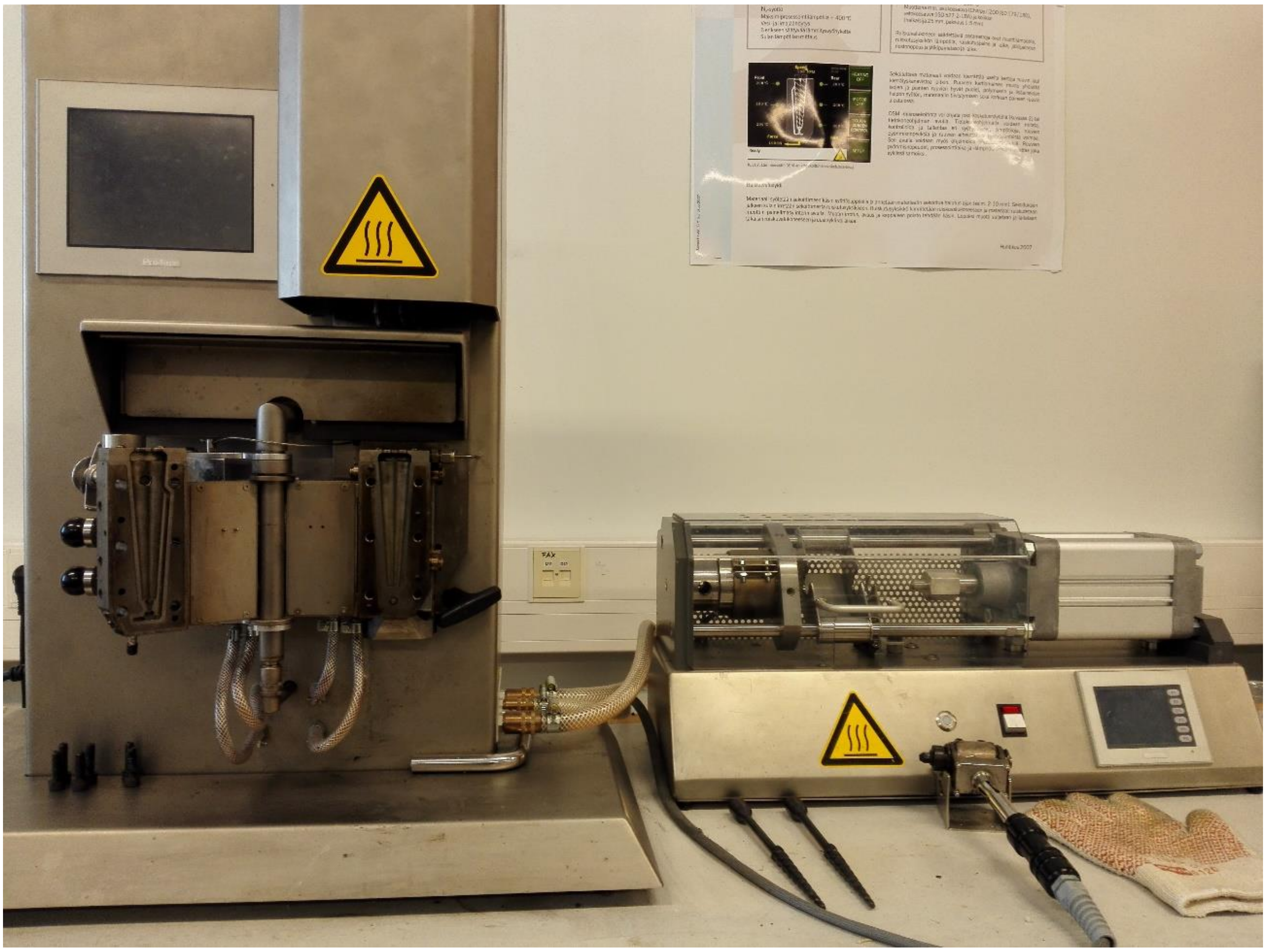


Figure 15. DSM Xplore TM 5 cm^3 compounder.

This mini compound is very versatile and convenient for producing samples instantly. Due to small volume of intake and batch size of input, for a shot it produces 1-2 samples for molding. Also molding it allowed by transferring the melt manually. While handling manually only one sample of quantity can be taken at a time. V-shaped co-rotating screw design packs polymer inside mold very well. But on other side the screws are very smooth in surface with circulating nature. Dispersion is mainly depends on the screw design. Due to no other option in screw changes, available screws and its existing design were used. On other hand high shear rate between the screw and barrel with mold temperature assume the qualitative mixing. The impact strength and SEM analysis the results were interpreted accordingly.

4. RESULTS AND DISCUSSION

Addition of 0.5% of CNTs is very challenging to disperse in polymer metrics. Only very few of them are able to reach their results by increasing 17% and 22% of elastic modulus and ultimate strength in result. Mechanical testing includes impact resistance, tensile resistance factor shows the toughness and brittleness of the material. Through which we can consider to the application properties for the proper sustainable use. In SEM image we can see the cavitations and the compatibility nature of polymer and matrix layer. How clearly packed and any porous, void and flaws can be detectable which is highly considerable during aerospace or defence application usage [31].

4.1 Impact Test

In the majority of the cases the mechanical strength will increases with incorporation of filler in polymer matrix. Also considering the results from the others research, fracture toughness is increased in nano composites [32].

Figure 16. CEAST make ‘RESIL 5.5’ Izod Impact tester.

Specimens are conditioned in laboratory condition at 23 ^{o}C. ISO D180 standard was used with ‘Izod’ un-notch pendulum type tester.

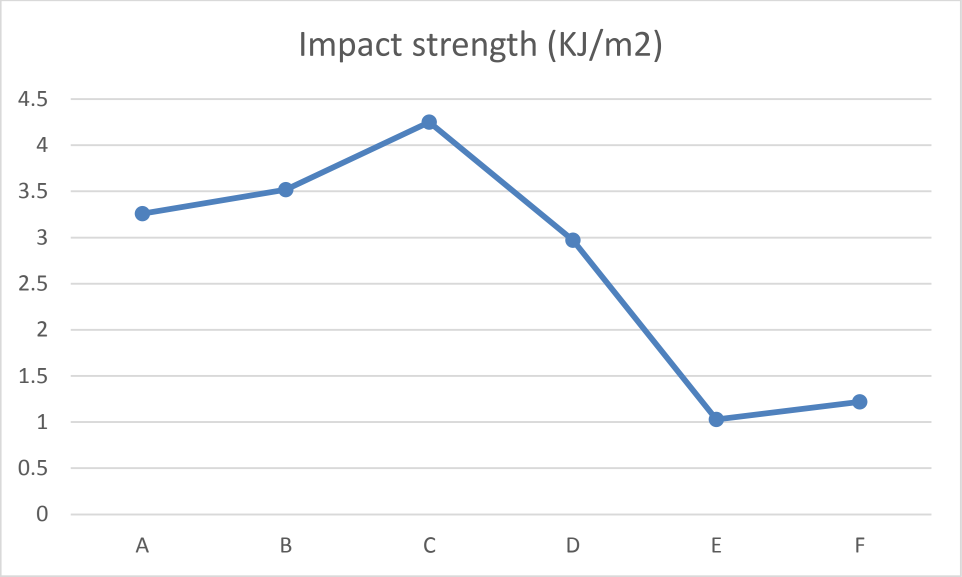


Figure 17. Impact strength result

Through above result we can clearly notice that the incorporation of pristine CNTs in nylon 66 matrix increase the impact strength. But the sonicated CNTs step down the result. Furthermore, also result decreased from sample ‘C’ to ‘E’ drastically. Sample ‘F’ sonicated CNTs showing a bit positive result by raising the strength. In overall pristine CNTs extruded through extruder is good toughness to sudden impact and comparable elastic nature in it. While in processing step noticed that extrusion process downstream holds vacuum system and long L/D ratio. Vacuum holds the pressure of 1-1.5 atmosphere which helps to take out the moisture and other volatiles presence. In this case chances of formic acid is very less. Because of the operation temperature maintained greater than formic acid boiling temperature. This will be removed & evacuated during the first four barrels in extruder processing unit zone. So no trace is expected. But it can be confirmed later through FTIR studies in generally. Regardless, in compounder situation, lack of vacuum system and other volatile substance may defect the samples. Even though, here temperature is higher than the formic acid there is no chance of formic acid, air & moisture getting out through barrel system during processing. The trace may left inside and chances of taking the same molten polymer to prepare test samples. Hence, the results were obtained very low due to air entrapment, moisture and volatile substance presence inside it.

4.2 Tensile Test

Tensile test is a simple mechanical test which explains the strength of the material when it's subjected under stress until it breaks or undergo permanent deformation. Instron 5967 model, universal testing machine is used to calculate the tensile strength of the prepared specimens as per ASTM D790 standard.

Figure 18. Instron 5967 universal testing machine.[33]

The load extension capacity is increased gradually to sample 'D' and drops. It means the sonicated CNTs with extrusion process has shown a importance in changes by increase its elastic nature of polymer matrix. Compounder technique is failed to maintain even the base level of value and rather to that, it decreased in results shows the more interesting part to study on this research.

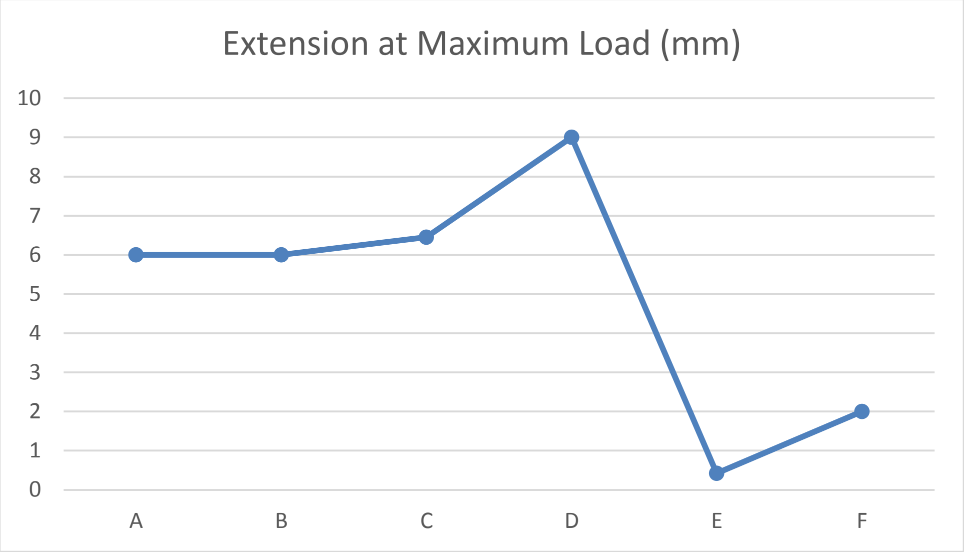


Figure 19. Tensile test result - Extension at Maximum load

The load extension capacity is increased gradually up to sample, ‘D’ and later it dropped. It means the sonicated CNTs (Sample ‘D’ and ‘F’) in matrix both results in good by great in compatibilization but shown very less changes to increase in strength and rigidity compare to other polymer filler interaction.

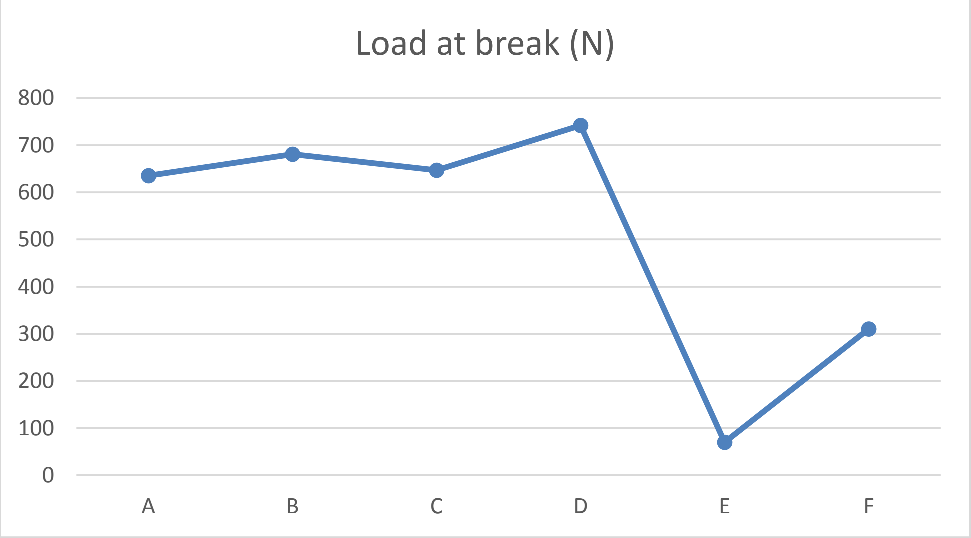


Figure 20. Tensile test result - Load at break

The maximum load withstand capacity is decreased to sample ‘C’ from virgin material and raised in sample ‘D’. Again the sonication of CNTs has shown its feature in changes to hold the load at maximum potential points.

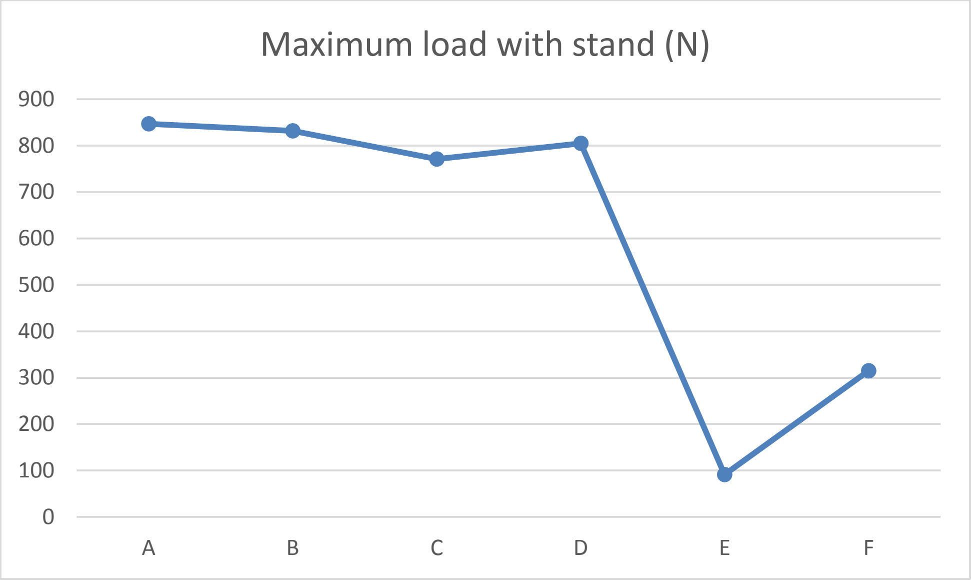


Figure 21. Tensile test result - Maximum load withstand

Through the above result, one common point can be easily noticed that the effect of sonication is helping somehow to rise the results in sample 'D' and Sample 'F'. Reason beyond the fall in values is quite similar to impact test results. It applicable the same reason here like impact test results. But for more in-depth, studies were taken into the molecular level, its arrangement & interaction of polymer filler matrix. Through SEM images results were determined the effects of formic acid, sonication and matrix - filler binding.

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

It is a technique used to acquire absorption and emission records when infrared waves are passed through the respected sample. Through this each material can be characterised. Example by identifying there functional groups, bonds and chairality of the structure.

For our studies "Bruker-Tensor 27" FTIR is used. Opus 6.5 updated software adjusted to Pike Attenuated Total Reflection (ATR) germanium engine. Initially best composition for the CNTs with KBR is found by trial and error method. It's noted that composition mix of 99% KBr and 1% CNTs will provide the required signals to detect the presence of CNT. Example, for 0.4160 g KBr we have added 0.0041g CNT to achieve the best result of it.

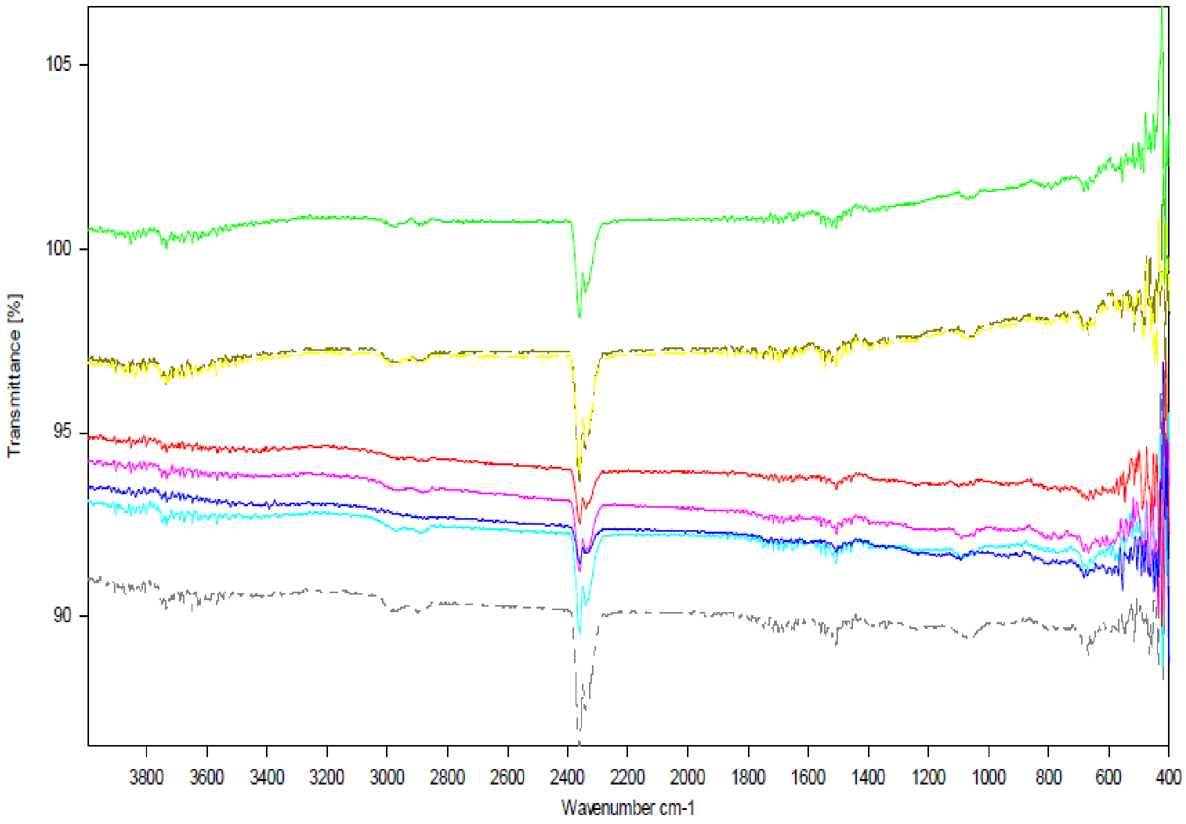


Figure 22. Sonicated CNT samples in water with no sign of functional groups attachment at 20th minute and higher different time intervals.[34] [35]

The back ground run is formed by pristine CNT. Later the sample contains sonicated CNT in water with polymer matrix is subjected to study the results. By observing the above result, we can't find any peak observation on various regions. So only the presence of OH confirms the effect of sonication on carbon nanotubes. Then the CH bond stretch, CO and NH functional group presence also confirms the active effect of molecule reacted with nylon 66 polymer matrix.

4.4 Differential scanning calorimetry (DSC)

In DSC and X-ray diffraction explained the increase in above 0.5wt% tends to decrease in mechanical properties. But in DSC heating curves, CNT and nylon 66 composite consist of two melting peaks. It had analysed through First (Tm^1) and secondary melting (Tm^2) peaks. Depending on Tm^1 and Tm^2 features exhibiting the thin lamellae formation, while cooling and melts the thicken crystals, while heating respectively. Increase in more than 0.5wt% CNTs adversely shows an effect on Tm^2 by lowering its temperature peak. Due to this effect, heat of fusion of Tm^1 increased. At maximum of 2wt% incorporated CNTs inside the nylon 66 matrix, formed CNTs networks tends to slow thickening of lamellars in nylon 66 spherulites initiated crystals and completely vanish of Tm^2 peak was observed and shown below [36].

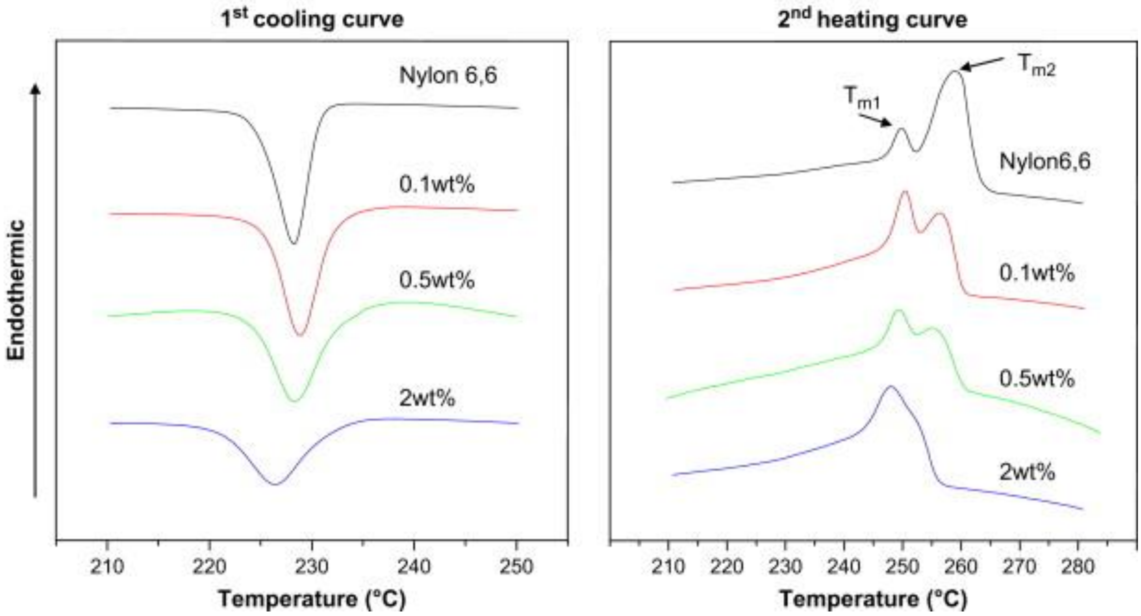


Figure 23. DSC curves of nylon 66 and CNTs at 10 °C/min ramp rate in non-isothermal condition.[36]

Sample A to F below shows the change in T_g value with respect to their morphological arrangements of CNTs in matrix.

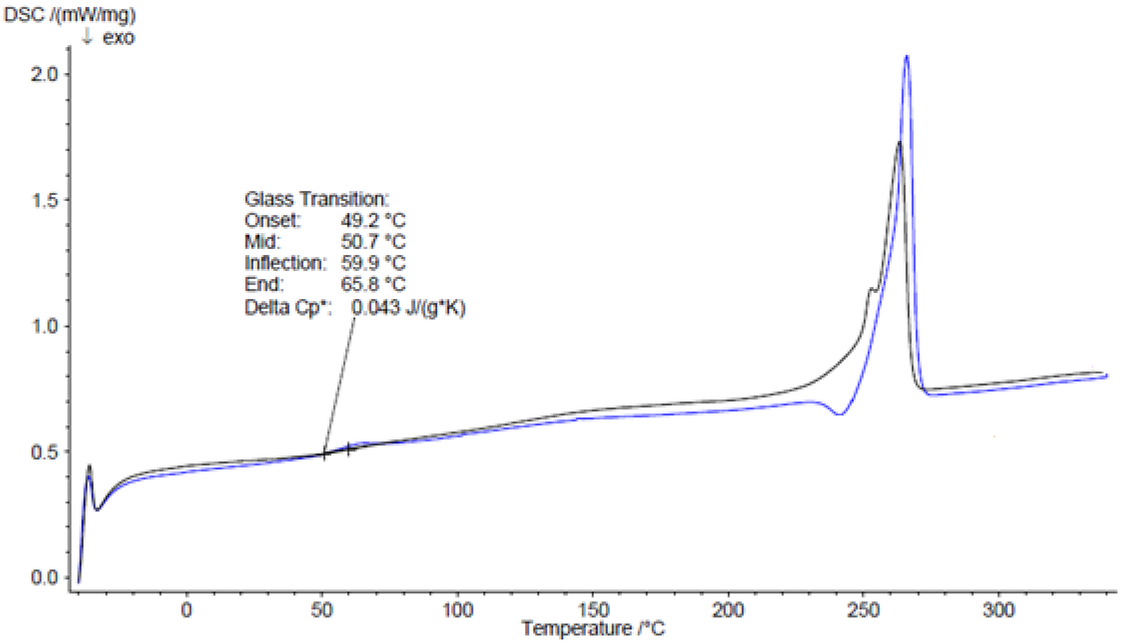


Figure 24. Sample 'A' results obtained from DSC.

From the above graph glass transaction of nylon 66 is increased by incorporating the CNTs in it. But while looking at sample ‘E’& ‘F’ the introduction of formic acid decreases the Tg and the mechanical properties excluding the processing technique. Other results like impact and tensile strength are also followed the same trend in these samples.

Table 3. DSC results of sample A, B, C, D, E and F.

Glass Transaction Parameters	**Sample ‘A’**	**Sample ‘B’**	**Sample ‘C’**	**Sample ‘D’**	**Sample ‘E’**	**Sample ‘F’**
Onset in ^{o}C	49.2	50.6	47.0	46.8	39.9	53.5
Mid in ^{o}C	50.7	53.7	56.0	53.0	39.7	44.6
Inflection in ^{o}C	59.9	57.4	63.5	56.1	30.8	42.7
End in ^{o}C	65.8	56.7	64.9	65.2	39.6	45.0
Enthalpy (Delta Cp), J/(g*K)	0.043	0.027	0.047	0.086	0.001	0.011

By considering the change in variable enthalpy result, it indicated that crystallinity increased with rise in enthalpy values and in some sample cases decreased in enthalpy is effected due to the presence of solvent and moisture.

4.5 Scanning electron microscope

Field emission gun scanning electron microscope (FEG-SEM) from the Zeiss ULTRA plus, German make is used to study the morphological behaviour and interaction of CNTs with nylon 66. Instrument can heat up to 1050 ^{o}C. Having very unique combination of detectors holding 127 eV resolution emitting energy detectors as shown below.

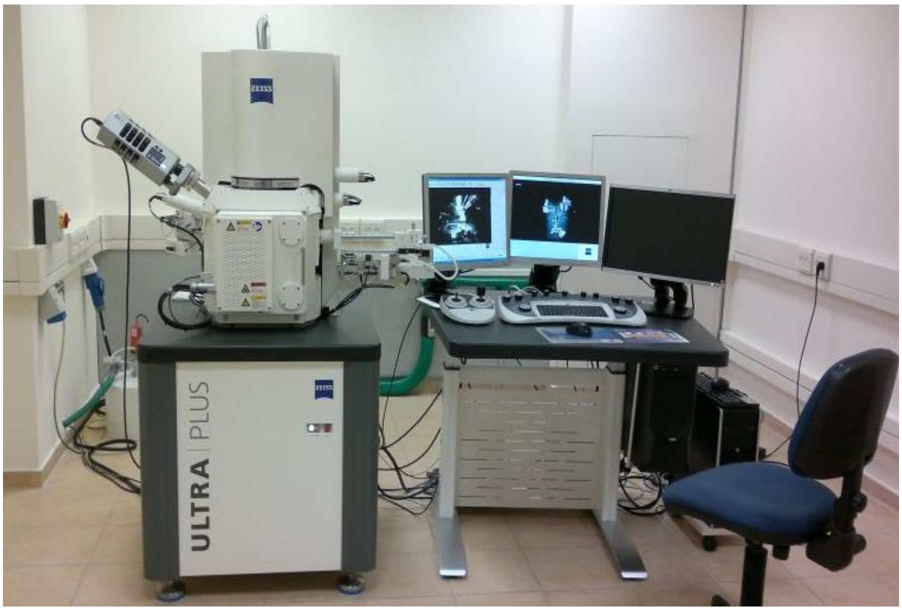


Figure 25. Field emission gun scanning electron microscope used in our studies.[37]

Samples ‘A’ virgin Nylon 66 and sample ‘B’ extruder passed materials are not subjected to SEM analysis. Sample ‘C’, nylon 66 with pristine CNTs in extruder, has recorded and SEM images are shown below. The SEM image indicates that the un-interacted polymer and layer formation between them. The holes and empty spaces are developed in between the particles.

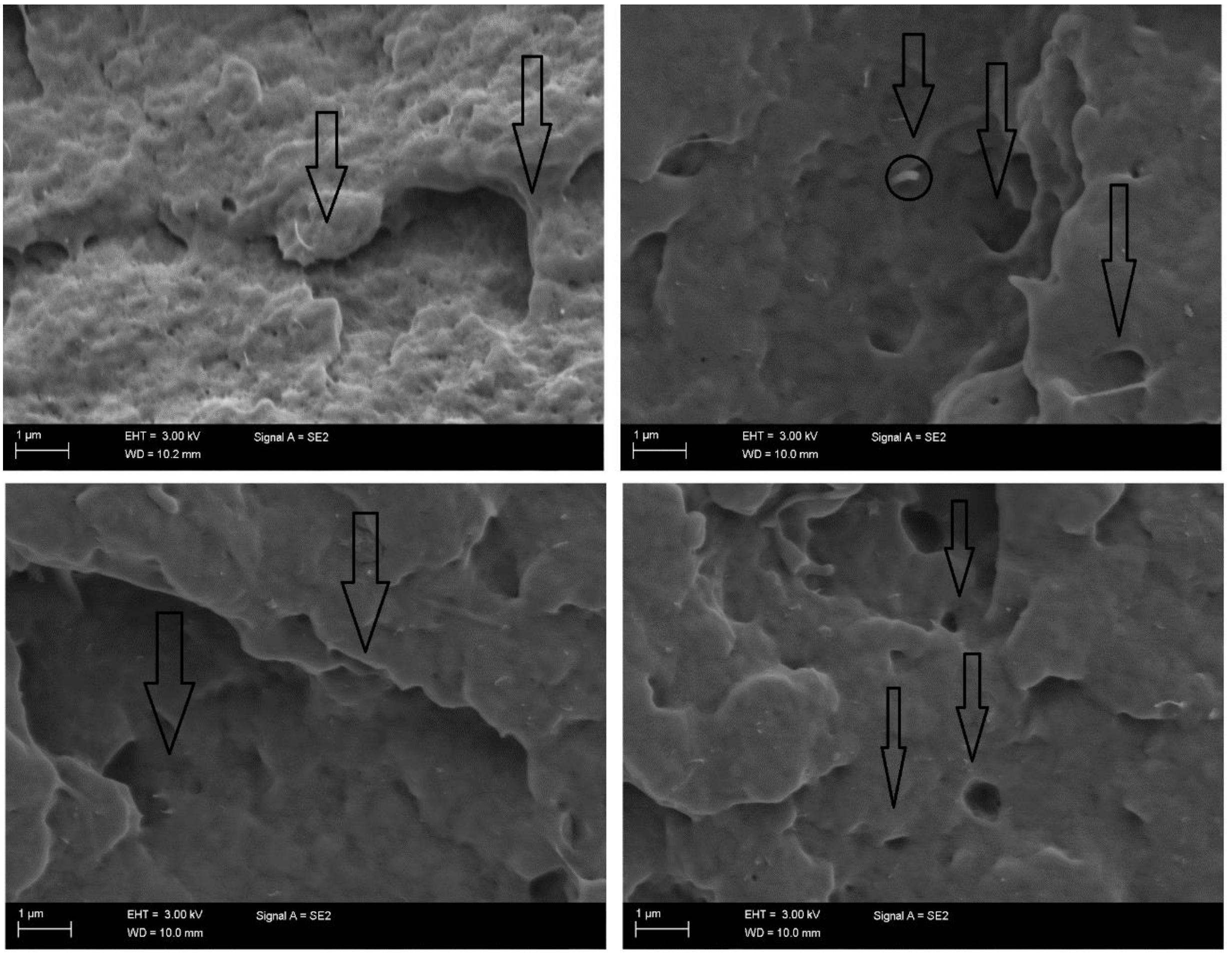


Figure 26. SEM images of Sample 'C' Nylon 66 with pristine CNT in extruder.

Un-interacted polymer were noticed in this observation highly. It indicated the melting the polymer by rising temperature or high speed rotation by applying shear force is not enough to disperse in this case. Vacuum pump for volatile substance was also not enough to control the holes and voids formation. In general during dispersion mixing and our studies, vacuum pump is fixed in metering section zone. As melting need to improve, vacuum pump is also be need in mixing section to overcome melting problem. Pristine CNTs were distributively mixed and quality of dispersion is examined through filter pressure value test.

Sample ‘D’ nylon 66 with water sonicated CNTs in extruder, has captured and shown below. From SEM images, it can see the more agglomerated CNTs particles which were not properly missile with matrix layer. However, the layer formation is controlled and particles are distributive mixed.

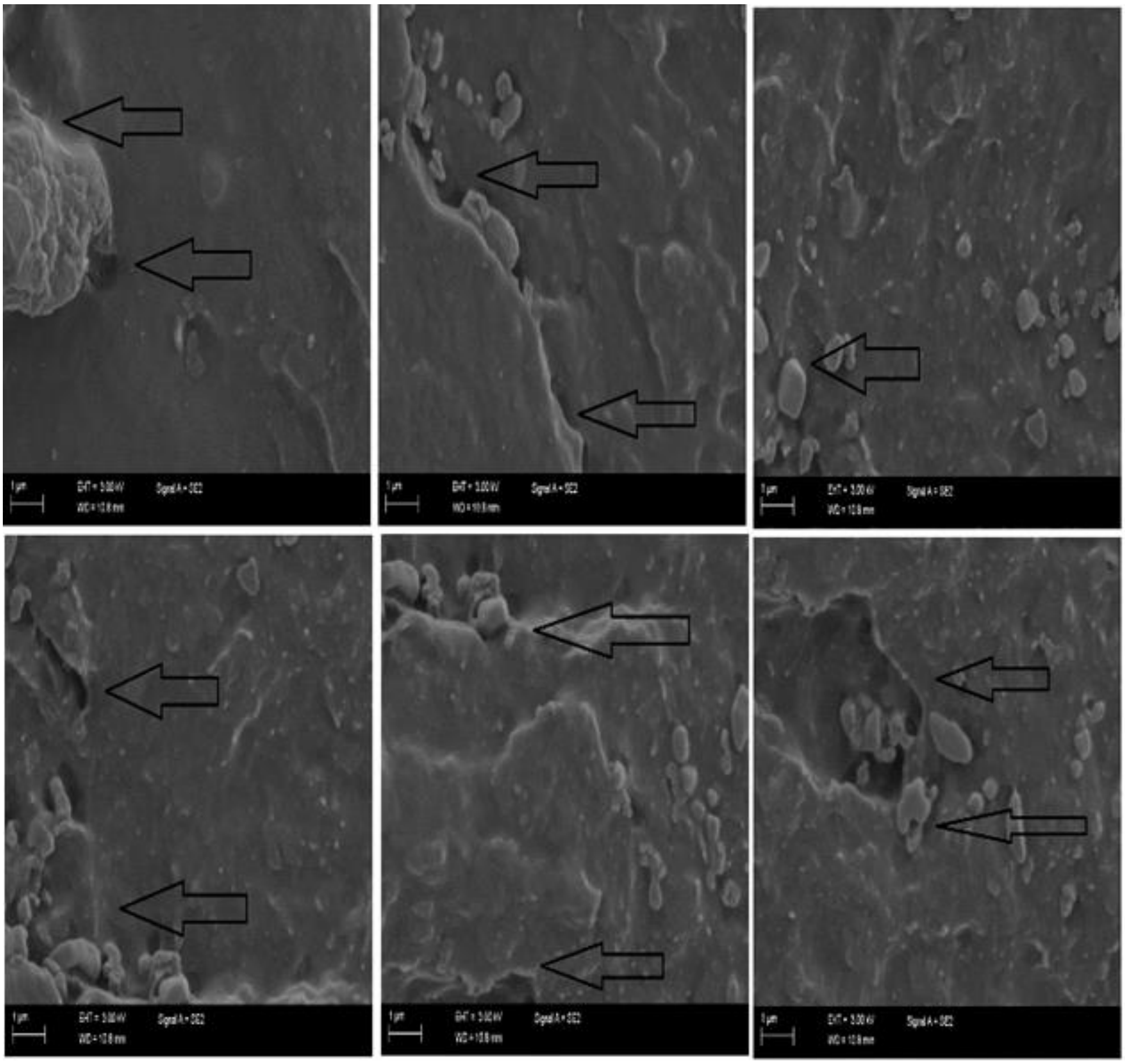


Figure 27. SEM images of Sample 'D' Nylon 66 with water sonicated CNTs in extruder.

The above samples were highly concrete with agglomeration of CNT groups. Problem in dispersion is noticed through the above images. Mixing elements and kneading elements need to placed more and in proper position avoid the cluster formation. Cluster free SEM images of sample ‘C’ comparing to Sample ‘D’ proves that the sonication was significantly impacts on CNTs and it results can be seen through these type of agglomeration formations. Even though obtained process and results were bad for the sample ‘D’, in later stages limitation were directly target to control and enhance the property.

Sample ‘E’, nylon 66 with pristine CNTs in compounder has captured and shown below. In the SEM image we can notice the more cavity or void formation and the layer formation due to formic acid residue. It drags the polymer when it subjected to heat while processing and created more void spaces. Even the depth of the layer is noticed widely. Compare to sample ‘C’, drawback of un-melted polymer were solved through this technique.

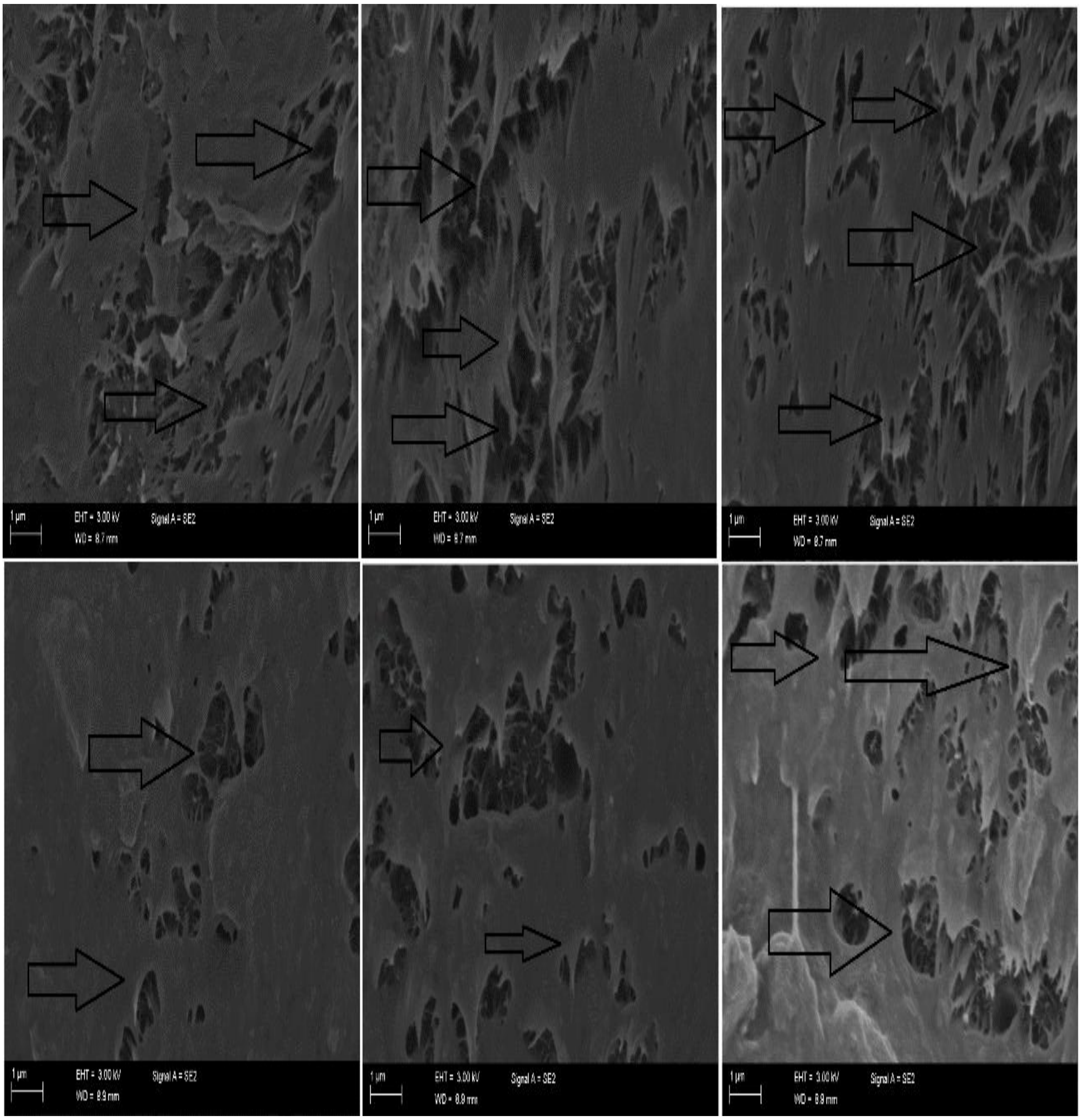


Figure 28. SEM images of Sample 'E' Nylon 66 with pristine CNTs in compounder.

Sample ‘F’, nylon 66 with sonicated CNTs in compounder has captured and shown below. In the given SEM image we can compare this result to sample ‘D’ and see the same agglomerated CNTs particles which were not properly missile with matrix layer. This may can resolve my mixing by higher shear force using dispersing elements extruder or proper screw channel in compounder.

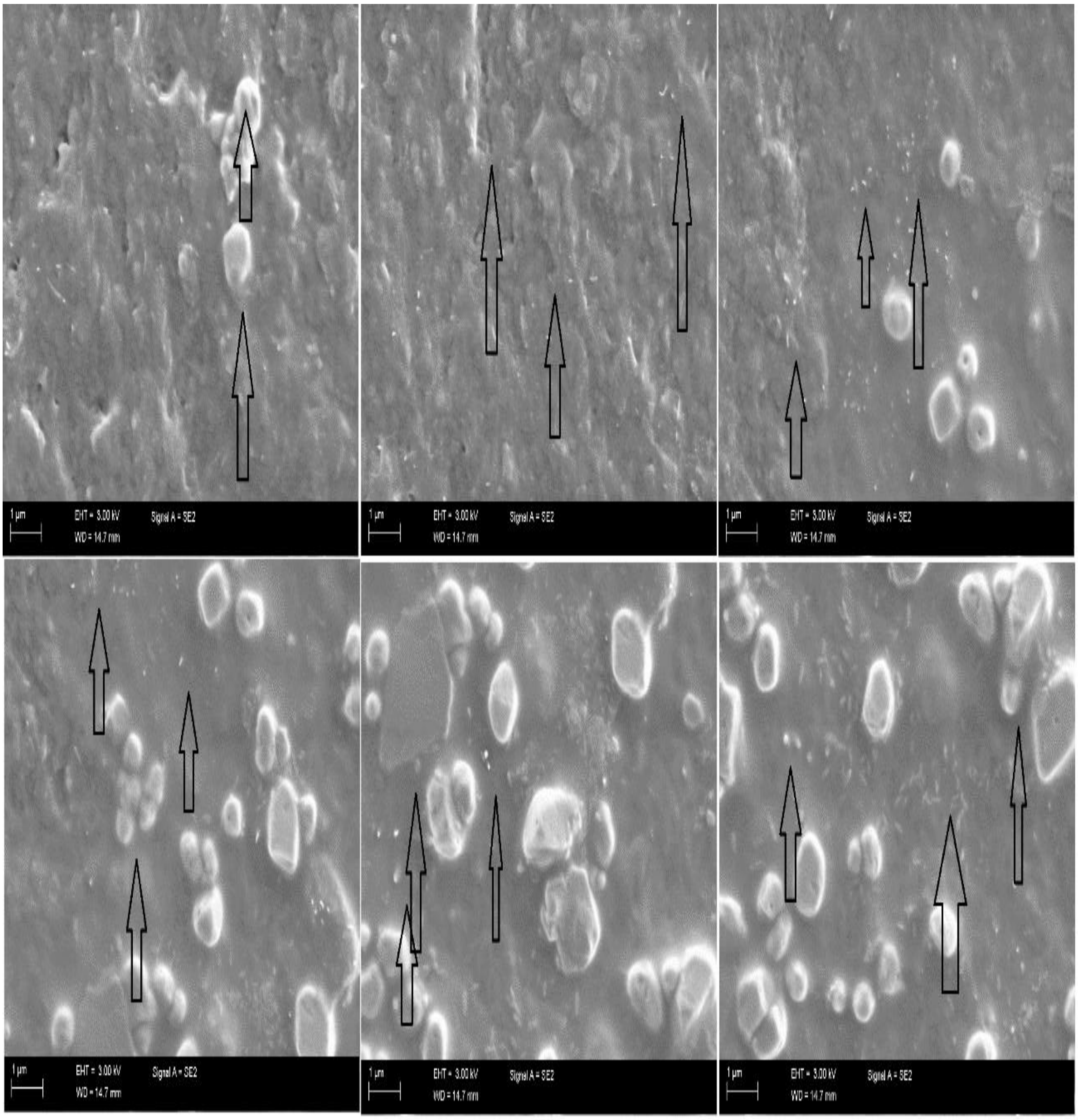


Figure 29. SEM images of Sample 'F' Nylon 66 with water sonicated CNTs in compounder.

Cluster free SEM images of sample ‘E, comparing to Sample ‘F’ with the same processing technique proves the sonication presence in sample ‘F’ and its impacts on CNTs result were observed.

4.6 Filter pressure value test

According to the European standard DIN EN 13900-5, pigments and extenders are measures through the dispersion quality using this test. The schematic control is shown below.

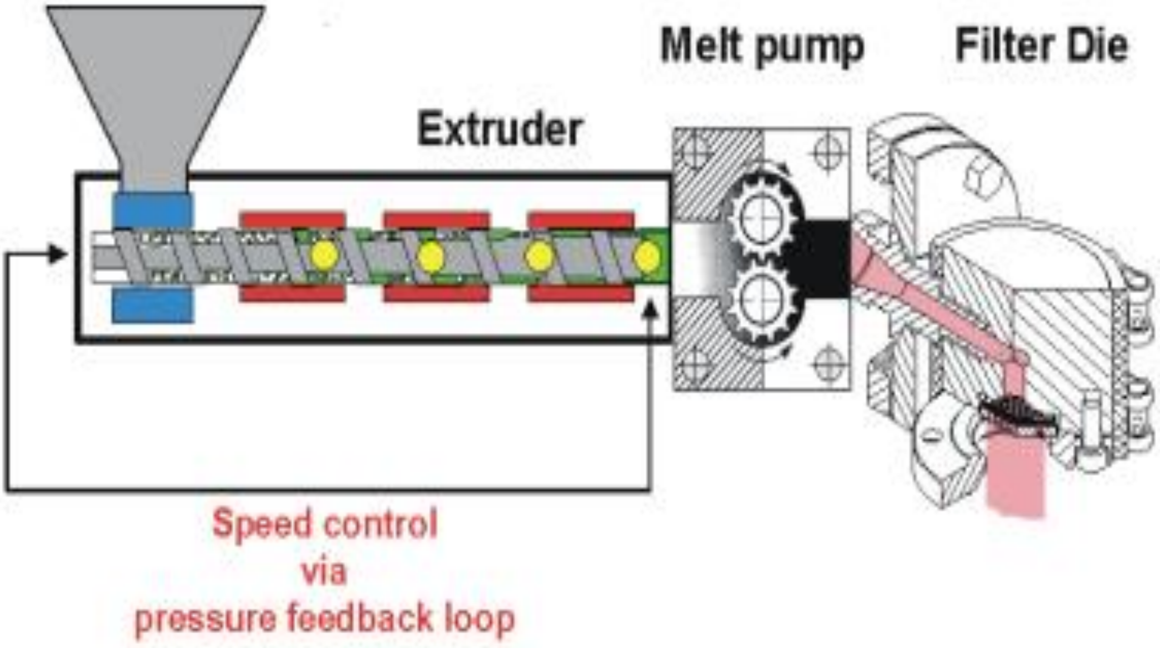


Figure 30. Schematic Layout of melt flow inside the filter pressure value testing machine.[38]

The filter pressure value (FPV) is defined as the increase of pressure per gram colorant, is nothing but passing the molten polymer in the different mesh size to see the size of the filler distribution with respect to applicable pressure and calculated using below equation. Results are recommended to note precisely to one decimal point. Units are measured in bar/g [35-38].

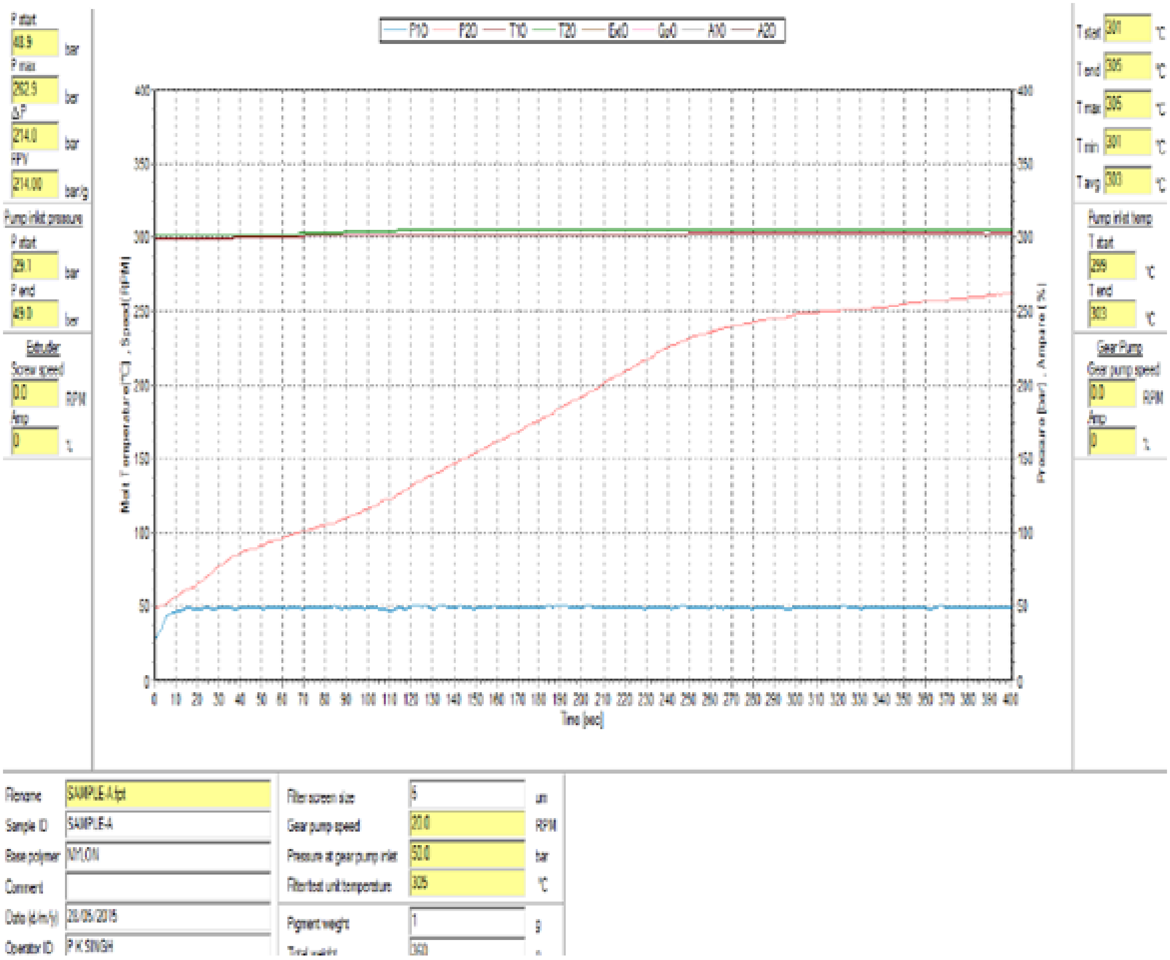
$$FPV = \frac{(Pmax - Ps)}{Mc}$$

where
FPV - Filter pressure value, [bar/g]
P_{max} – Maximum pressure, bar
P_s – Start pressure, bar
M_c – quantity of colorant, gram

During the test, each sample are taken to 90 g and concentration is reduced by adding them to 270 g of virgin polymer matrix and moisture content is recorded respectively. Each batch size of total weight 360 g taken for all the conducted experiments. Calculated amount of material was transfer to 25 L/D ratio single screw extruder. Through melt / gear pump melt is passed through 100 and 5 micron mesh inside the filter die. To maintain the pressure overall through experiment, the virgin polymer matrix is passed first and recorded as a sample or background date for all the samples. Once it get stabilize, the original sample to analyze is passed and

FPV results are recorded. FPV results were obtained through melt temperature and its pressure versus time graph shown below.

For the sample ‘C’, nylon 66 with pristine CNTs in extruder, holds 0.35% of moisture content during FPV experiment time. Pump inlet pressure starts and ends from 29.1 to 49 bar. Pressure value at screen start at 48.9 bar and max raised to 214 bar. FPV value is calculated and shown as 214 bar/g.



P start 48.9 bar
P max 262.9 bar
ΔP 214.0 bar
FPV 214.00 bar/g

Pump inlet pressure
P start 29.1 bar
P end 49.0 bar

Extruder
Screw speed 0.0 RPM
Amp 0 %

T start 301 °C
T end 305 °C
T max 305 °C
T min 301 °C
T avg 303 °C

Pump inlet temp
T start 299 °C
T end 303 °C

Gear Pump
Gear pump speed 0.0 RPM
Amp 0 %

Filename SAMPLE-A.fpt
Sample ID SAMPLE-A
Base polymer NYLON
Comment
Date (d/m/y) 20/05/2015
Operator ID P K SINGH

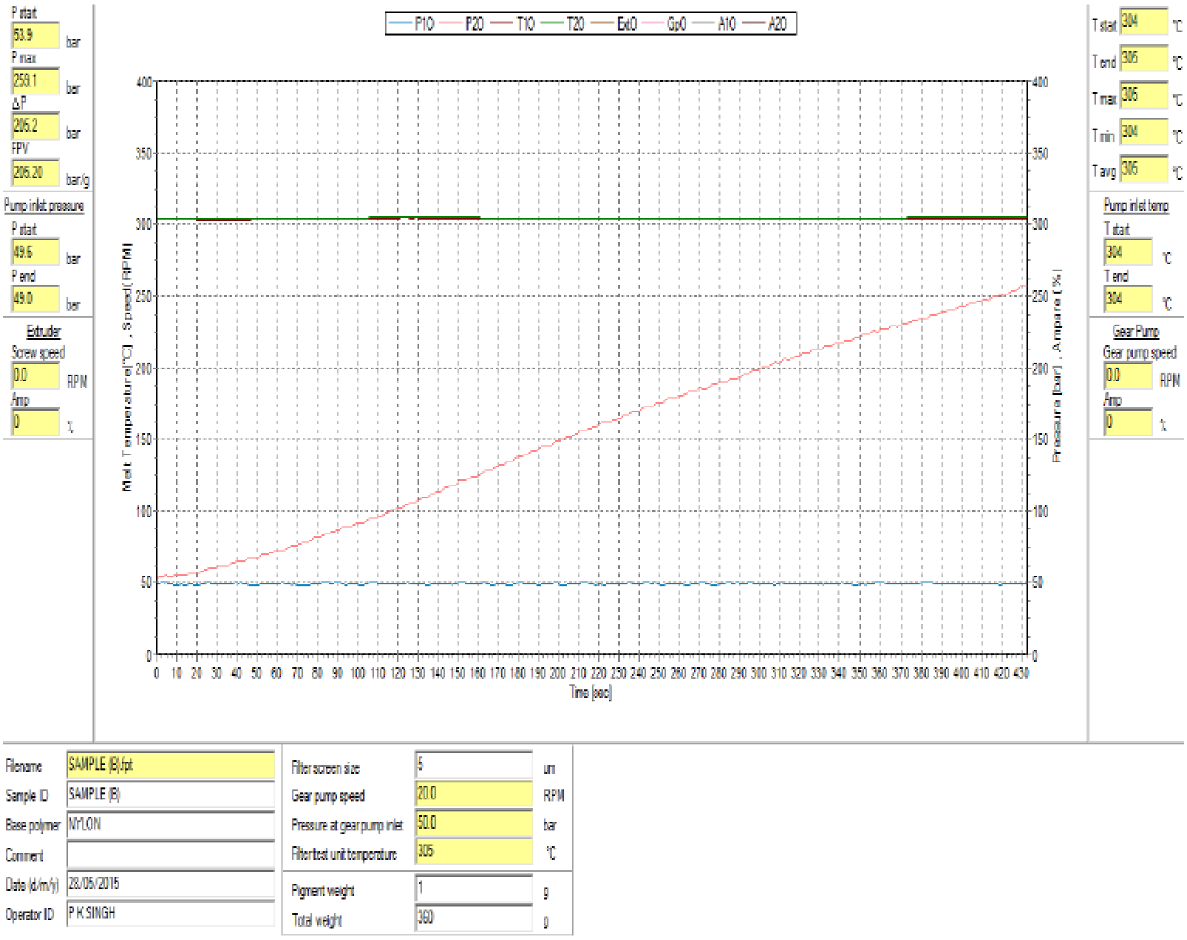
Filter screen size 5 um
Gear pump speed 20.0 RPM
Pressure at gear pump inlet 50.0 bar
Filter test unit temperature 305 °C

Pigment weight 1 g
Total weight 360

Figure 31. Sample ‘C’ Nylon 66 with pristine CNTs in extruder - FPV result.

The blue color line indicated the run of virgin polymer matrix before to run the sample ‘C’. It should be considered as a reference or background data. Analyzing the above result, melt temperature and pressure start to increase with respect to increase in time. It indicates that polymer melt is dragged until the 400 seconds, then the un-melted polymer and filler agglomerates completely block the mesh. It shows the poor dispersion quality and trace of CNT is not be regularized. High FPV value indicated rise in pressure and blockage of mesh.

For the sample ‘D’, nylon 66 with water sonicated CNTs and extruded, holds 0.21% of moisture content during the experiment time. Pump inlet pressure starts and ends from 49.6 to 49 bar. Pressure value at screen start at 53.9 bar and max raised to 259.1 bar. FPV value is calculated and shown as 205 bar/g.



P start 53.9 bar

P max 259.1 bar

ΔP 205.2 bar

FPV 205.20 bar/g

Pump inlet pressure

P start 49.6 bar

P end 49.0 bar

Extruder

Screw speed 0.0 RPM

Amp 0 %

T start 304 °C

T end 305 °C

T max 305 °C

T min 304 °C

T avg 305 °C

Pump inlet temp

T start 304 °C

T end 304 °C

Gear Pump

Gear pump speed 0.0 RPM

Amp 0 %

Filename SAMPLE (B).fpt

Sample ID SAMPLE (B)

Base polymer NYLON

Comment

Date (d/m/y) 28/05/2015

Operator ID P K SINGH

Filter screen size 5 um

Gear pump speed 20.0 RPM

Pressure at gear pump inlet 50.0 bar

Filter test unit temperature 305 °C

Pigment weight 1 g

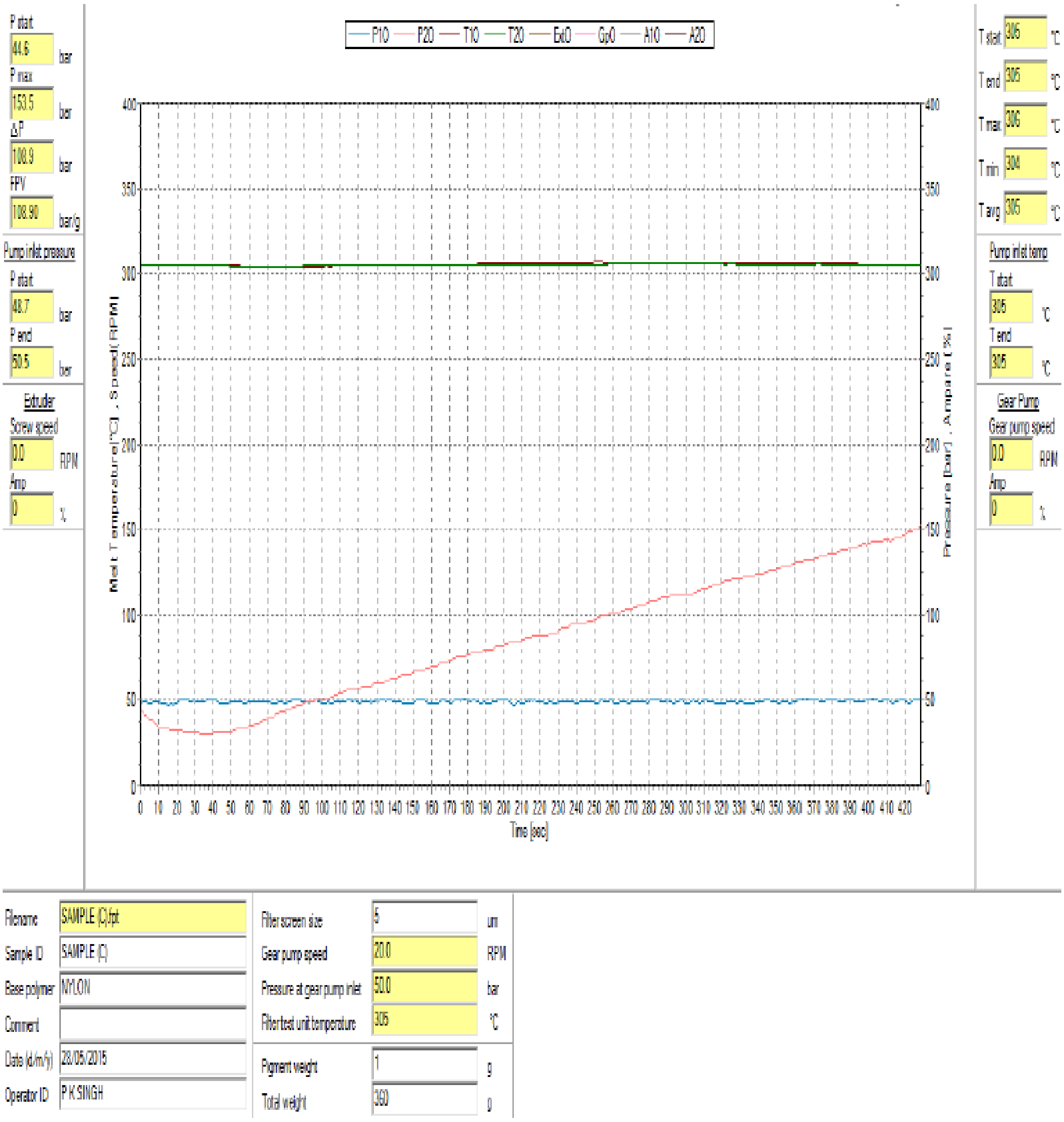
Total weight 360 g

Figure 32. Sample 'D' Nylon 66 with water sonicated CNTs in extruder - FPV result.

The blue color line indicates the background data of virgin polymer matrix before to run the sample ‘D’. Analyzing the above result, melt temperature and pressure start to increase with respect to increase in time. It indicates that polymer melt is dragged until the 430 seconds, then the un-melted polymer and filler agglomerates completely blocks completely block the mesh. It also shows the poor dispersion quality and trace of CNT is not be regularized. High FPV value indicated rise in pressure and blockage of mesh. Dispersion quality is poor than the sample ‘C’.

For the sample ‘E’, nylon 66 with pristine CNTs in compounder, holds 0.47% of moisture content during the experiment time. Pump inlet pressure starts and ends from 48.7 to 50.5 bar.

Pressure value at screen start at 44.6 bar and max raised to 153.5 bar. FPV value is calculated and shown as 108.9 bar/g.



P start 44.6 bar
P max 153.5 bar
ΔP 108.9 bar
FPV 108.90 bar/g

Pump inlet pressure
P start 48.7 bar
P end 50.5 bar

Extruder
Screw speed 0.0 RPM
Amp 0 %

T start 306 °C
T end 305 °C
T max 306 °C
T min 304 °C
T avg 305 °C

Pump inlet temp
T start 305 °C
T end 305 °C

Gear Pump
Gear pump speed 0.0 RPM
Amp 0 %

Filename SAMPLE (C).fpt
Sample ID SAMPLE (C)
Base polymer NYLON
Comment
Date (d/m/y) 28/05/2015
Operator ID P K SINGH

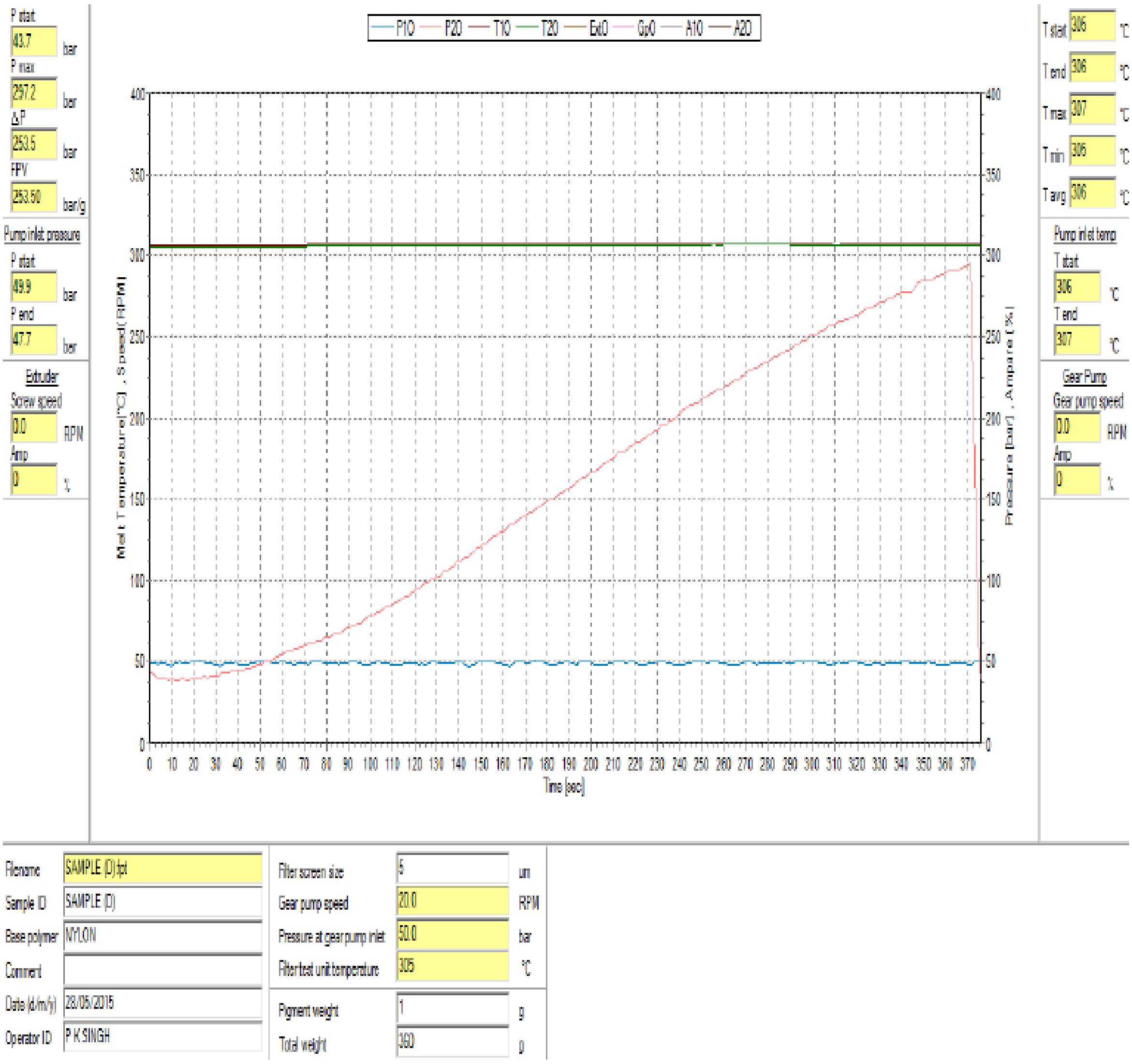
Filter screen size 5 um
Gear pump speed 20.0 RPM
Pressure at gear pump inlet 50.0 bar
Filter test unit temperature 305 °C

Pigment weight 1 g
Total weight 360 g

Figure 33. Sample 'E' Nylon 66 with pristine CNTs in compounder - FPV result.

Analyzing the above result, melt temperature and pressure start to decrease initially with respect to increase in time. So it shows that the only pure polymer part inside the sample mixture was dragged out from the melt pump in this case. Pure matrix part is extruded until the 100 second of run time, then the original mixture is passing through the output. Thus the pressure was low as material is free flowing through the mesh. But comparing to previous samples of ‘C’ and ‘D’ the mesh was blocked inside when they started to flow. It indicates that polymer melt is dragged until the 420 seconds, then the un-melted polymer and filler agglomerates completely blocks the mesh. It also shows the good dispersion quality and trace of CNT in the mixture. Low FPV value indicated less in pressure and blockage of mesh. Dispersion quality is higher than the sample ‘C’ and ‘D’ in this case.

In sample ‘F’, nylon 66 with pristine CNTs in compounder, holds 0.33% of moisture content during the experiment time. Pump inlet pressure starts and ends from 49.9 to 47.7 bar. Pressure value at screen start at 43.7 bar and max raised to 252.5 bar. FPV value is calculated and shown as 253.5 bar/g.



P start 43.7 bar
P max 297.2 bar
ΔP 253.5 bar
FPV 253.50 bar/g

Pump inlet pressure
P start 49.9 bar
P end 47.7 bar

Extruder
Screw speed 0.0 RPM
Amp 0 %

T start 306 °C
T end 306 °C
T max 307 °C
T min 305 °C
T avg 306 °C

Pump inlet temp
T start 306 °C
T end 307 °C

Gear Pump
Gear pump speed 0.0 RPM
Amp 0 %

Filename	SAMPLE (D).tpt
Sample ID	SAMPLE (D)
Base polymer	NYLON
Comment	
Date (d/m/y)	28/05/2015
Operator ID	P K SINGH

Filter screen size	5	um
Gear pump speed	20.0	RPM
Pressure at gear pump inlet	50.0	bar
Filter test unit temperature	305	°C
Pigment weight	1	g
Total weight	360	g

Figure 34.Sample 'F' Nylon 66 with water sonicated CNTs in compounder - FPV result.

Analyzing the above result, melt temperature and pressure start to decrease initially with respect to increase in time like sample ‘E’. So it shows that the only pure polymer part inside the sample mixture was dragged out from the melt pump initially. Pure matrix part is extruded until the 50 second of run time, then the original mixture is passing through the output. But later on the pressure shoots up high as material is restricted to flowing through the mesh. Comparing to previous samples of ‘E’, Sample ‘F’ was blocked soon inside the mesh. It indicates that polymer melt is dragged until the 370 seconds, then the un-melted polymer and bigger filler agglomerates completely blocks the mesh. It also shows the good dispersion quality and trace of CNT in the mixture. Low FPV value indicated less in pressure and blockage of mesh. Dispersion quality is higher than the sample ‘C’ and ‘D’.

5. CONCLUSION

In this study, carbon nanotubes were introduced to Nylon 66 polymer by subjecting them in to two different processing techniques to achieve the maximum performance from them. To achieve better performance CNT should properly disperse and adhere with polymer matrix and CNTs are not easily bound in nature to stick with nylon. For this reason, CNTs are modified with sonochemical pre-treatment and studied. Samples were prepared from extrusion and compounding processing techniques were analyzed by mechanical and morphological studies. Quality of dispersion is analyzed from an advanced technique called filter pressure value test.

As the result of work:

- *The effect of sonication pretreatment on carbon nanotube filler in nylon 66 polymer matrix was studied.*

  Carbon nanotubes fluffy characteristic made incorporation very difficult. Sonication pre-treatment helps in wetting and good compatibility between filler and matrix. Sonication not only helps on wetting, also during processing it reduces sample texture roughness and brittleness compare to pristine CNT samples. But activation through water media as a solvent in sonication process was fail. Noticed that not easily to beak water molecules through ultrasonic energy treatment. May be addition of anionic surfactants (Eg., sodium dodecylbenzene sulfonate), initiators and other activators can be a possible way to evaluate the sonication process efficiently. Also by adopting cooling system during sonication process, may help to control the raise in water temperature above 48oC. So that sonication time will take above 20 minutes and study in-depth.

- *The effect of solvent and its ease in processing technique was studied.*

  Indeed, many of other studies provides the data of various solvents can be used, except formic acid and dissolution of polymer on to it technique. Through this work with the new idea which ends with a negative results which also gave a basic to not to continue with formic acid in future studies. If it’s really needed, then formic acid can be regenerated and re-use while kept for drying after the dispermat process. It save larger cost of investing on formic acid in industrial scale.

- *The effect of two different processing technology on samples was studied.*

  It compares the most effective level of processing technology to choose among TSE and compounder. First with Pristine and SCNTs samples ‘C’ and ‘D’ are prepared using TSE. By comparing those with Pristine and SCNTs samples ‘E’ and ‘F’ which were subjected to high speed mixer and compounded are studied in this research.

  It clearly shows the effect of screw configuration is highly important in these kind of processing level of nano filler material. Proper kind of mixing, melting, and metering zone elements are recommended to improve quality of dispersion and distribution of filler in matrix. Even tough, vacuum pressure pump usage during extrusion process doesn’t control moisture level more effectively, importance of vacuum pump is shown and introduction of one more vacuum pump in mixing zone controls moisture efficiently than before. Screw design configuration work is newly introduced in this work which is not commonly available with design of experiment in extrusion process.

  Further to that, instead of taking sample to manual breakage after drying formed from high speed mixer or dispermat experiment, it could be good to introduce to ball mill for crushing and minimizing the size of agglomerates. So that, if the surface was attached and active with functional group won’t escape nicely.

  Another way to improve the mix by introducing the processing aid like wax, oil and stearate can also be add by studying further.

  Indeed, while preparing the master batch during high speed mixer decrease in CNT content or percentage in master batch can also lead good results. It leads easy to process in level of quality, also can be change in screw design with appropriate suitable elements.

6. ABSTRACT

The overall aim of the work is to observe the effect of sono-chemical pretreatment on carbon nanotubes, its dispersion quality and develop the suitable method to incorporate carbon nanotubes in nylon 66 polymer for better applications. The effect of sonochemical treatment majorly studied and using formic acid as a solvent which suitable to matrix material, also its saturation peak point with respect to the selected base polymer, 'nylon 66'. Even though amount of work done on CNT are extensive from past decays on various polymer but using nylon 66 as a matrix material was notices less in work. We have conducted this project in different methods of views to achieve better and successful results. Many researchers are done through with their different objective prospect for the similar composition. Here taken this in a way to study the CNTs behaviors when they get functionalized with water medium in sonication method and concentrated on the processing methods used to disperse the CNTs in matrix. For which we have used 'twin screw extrusion' (TSE) process and 'high speed shear mixer' (HSSM) to study. Also the way of technique to find the dispersion quality by using 'Filter pressure value' test (FPV) is newly introduced. Multiple steps are adopted to develop a better dispersion quality. Mechanical testing measures and characterize the overall performance of the prepared samples. As first and far most difficult part of this project looks towards mixing of CNTs into polymer matrix has influences us to incorporate the optimal level of filler in matrix to get high performance in output result. Different parameters and change in sequential parameters applied to obtained results were compared. Processing techniques values are looked together by comparing their results. Effect of sonication pretreatment, introduction of formic acid to form master batch for compounding and extrusion process were studies. To sum up, in results sonication done through water media was failed. Water molecules are not easily breakable through sonication energy and enough to develop functional groups to attach on CNTs through water molecules. Also through this research, reader can see what not to do and not to repeat the same process to get fail result in work for future studies. It's almost towards a negative result impact achievement. But in a positive way of look, it contribute to the further development and open the various other paths to continue this research to take forward. However, current work showed its importance at the initial stage of the research.

Keywords: CNTs, Dispersion, Nano composites, Sonochemical pretreatment, Twin screw extrusion, Compounder.

KOKKUVÕTE

Käesoleva magistritöö eesmärgiks oli selgitada sono-keemilise eeltöötluse mõju süsinik nanotorude dispersiooni omadustele nailon 66 maatriksis. Selle töö teoreetilises osas tutvuti Nanotorude töötlemis meetoditega erinevate polümeeride nanokomposiitide saamisel ja nende iseloomustamise võimalusi, kuid polüamiid 66 osutus harva kasutatavaks materjaliks. Vastavalt teiste autorite poolt varem teadusajakirjades publitseeritud artiklites leiduvatele erinevatele meetoditele valisime süsinik-nanotorude funktsionaliseerimiseks sonokeemilise eeltöötluse vesilahuses ja dispergeerimiseks maatriksisse esialgse töötlemise ülikiirete pööretega mikseris kompaundi standard partii saamiseks ja edasise töötlemise kahetolises kompaunderis polüamiid 66-ga. Sellise mitmeastmelise meetodi eeliseks pidasime erinevate parameetrite ühildamist ja otsest muutmise võimalust parima kompaundi saamiseks.Valitud meetodi peamiseks probleemiks kujunes töödeldud nanotorude segamine maatriksiga ja täiteaine optimaalse koguse selgitamine.Tulemuste arutelu käsitleb erinevate meetodite kasutamisel saadud kompaundide iseloomustamist FTIR-spektroskoopia, DSC, SEM mikroskoopia ja füüsikalis-mehaaniliste näitajate kaudu. Esmakordselt kasutasin dispersiooni hindamiseks materjali filtreerimisel tekkivat surve suuruse testi. Analüüsi tulemused ei kinnita üheselt sono-keemilise effekti olemasolu kuid tehtud töö põhjal jõudsin järeldusele, kuidas muuta kasutatud meetodit, kui jätkata uurimist samade materjalidega.

Keywords: CNTs, Dispersioon, Süsinik nanotorud, Sono-keemiline töötlemine, Ülikiirete Pööretega mikser, Kompaundimine.

7. REFRENCES

1. Prasek J, Drbohlavova J, Chomoucka J, Hubalek J, Jasek O, Adam V, et al. Methods for carbon nanotubes synthesis—review. Journal of Materials Chemistry. 2011. p. 15872.

2. Radushkevich L V., Lukyanovich VM. No Title. Zh Fiz Khim,. 1952;26:88–95.

3. A. Oberlin, M. Endo, T. Koyama. J. Cryst Growth. 1976;32:335–49.

4. Harris PJF. Harris, Peter J. F.. (2009). Carbon Nanotube Science - Synthesis, Properties and Applications - 1.5 Who Discovered Carbon Nanotubes?. Cambridge University Press. Carbon Nanotube Science - Synthesis, Properties and Applications [Internet]. Cambridge University Press; 2009 [cited 2015 Apr 13]. Available from: http://app.knovel.com/hotlink/pdf/id:kt009AQ5FB/carbon-nanotube-science/who-discovered-carbon

5. Wang X, Li Q, Xie J, Jin Z, Wang J, Li Y, et al. Fabrication of ultralong and electrically uniform single-walled carbon nanotubes on clean substrates. Nano Lett. 2009;9(9):3137–41.

6. Scientists delve deeper into carbon nanotubes [Internet]. [cited 2015 Apr 13]. Available from: http://missiontomorrow.tv/scientists-delve-deeper-into-carbon-nanotubes-physicsworld-com/

7. Hilding J, Grulke E a., George Zhang Z, Lockwood F. Dispersion of Carbon Nanotubes in Liquids. J Dispers Sci Technol [Internet]. 2003;24(1):1–41. Available from: http://www.tandfonline.com/doi/abs/10.1081/DIS-120017941

8. Prasek J, Drbohlavova J, Chomoucka J, Hubalek J, Jasek O, Adam V, et al. Methods for carbon nanotubes synthesis—review. J Mater Chem. 2011;21(40):15872.

9. Vuoristo P. Thin Film Technology (lecture notes). Tampere, Finland; 2013.

10. Hofmann M, Glückert JT, A.Högele. Growth of carbon nanotubes by chemical vapor deposition [Internet]. [cited 2015 Apr 10]. Available from: http://www.nano.physik.uni-muenchen.de/research/rep11/index.html

11. Bedewy M, Meshot ER, Hart a. J. Diameter-dependent kinetics of activation and deactivation in carbon nanotube population growth [Internet]. Carbon. 2012. Available from: http://www.sciencedirect.com/science/article/pii/S0008622312005702

12. Dr. Noorhana Yahya. Advanced structured materials. Carbon and Oxide Nanostructures: Synthesis, Characterisation and Applications. Springer Science & Business Media; 416 p.

13. Gulfem A, Ozgultekin O. MASTER ' S THESIS Characterization of Carbon Nanotube Doped Carbon Fiber Polymer Composites [Internet]. Luleå University of Technology; 2012. Available from: https://pure.ltu.se/portal/files/37029356/LTU-EX-2012-36998244.pdf

14. Vajtai Robert. Springer Handbook of Nanomaterials. Houston, TX 77005-1827, USA; 1257 p.

15. Liu C-X, Choi J-W. Improved Dispersion of Carbon Nanotubes in Polymers at High Concentrations. Nanomaterials. 2012;2(4):329–47.

16. Sonochemical [Internet]. [cited 2015 Apr 11]. Available from: http://en.wikipedia.org/wiki/Sonochemistry

17. Yang K, Yi ZL, Jing QF, Yue RL, Jiang W, Lin DH. Sonication-assisted dispersion of carbon nanotubes in aqueous solutions of the anionic surfactant SDBS: The role of sonication energy. Chinese Sci Bull. 2013;58(17):2082–90.

18. Wikipedia. Nylon 66 [Internet]. [cited 2015 Apr 21]. Available from: http://en.wikipedia.org/wiki/Nylon#Chemistry

19. Estructura Q. Nylon 66 [Internet]. [cited 2015 Apr 21]. Available from: http://www.eis.uva.es/~macromol/curso05-06/nylon/Nylon_file/page0002.htm

20. H.H. Yang. Handbook of Fiber Chemistry [Internet]. 3rd ed. Menachem Lewin/TUT e-library, editor. [cited 2015 Apr 21]. Available from: https://www.tut.fi/ms/muo/vert/10_reinforcing_materials/textile_production_nylons.htm

21. Formic acid [Internet]. [cited 2015 May 24]. Available from: http://www.ekta-international.com/formic-acid.html

22. Hielscher Sonicator [Internet]. [cited 2015 Aug 8]. Available from: http://www.hielscher.com/i1000_p.htm

23. Urbanski K, Platek B, Falat T. Novel Method for CNTs Dispersion in Fluids. 10th Conf Electron … [Internet]. 2010;(September):22–5. Available from: http://lipec.info/pdf/201003.pdf

24. MYR rotational viscometer [Internet]. [cited 2015 Aug 8]. Available from: http://viscotech.es/viscometer_vr3000.php

25. MYR rotaional viscometer [Internet]. [cited 2015 Aug 8]. Available from: http://www.myr.com.es/pdf/viscosimetro_ang.pdf

26. Huang YY, Terentjev EM. Dispersion of carbon nanotubes: Mixing, sonication, stabilization, and composite properties. Polymers (Basel). 2012;4(1):275–95.

27. Dissolver DISPERMAT [Internet]. [cited 2015 May 1]. Available from: http://www.vma-getzmann.com/english/products_for_lab_and_pilot_plant_/dissolver/dissolver_0_935_1722_2484.html

28. Nanoparticles dispersion process [Internet]. [cited 2015 May 26]. Available from: http://www.ipat.tu-bs.de/forschung/arbeitsgruppen/dispergieren-beschichtendispersing-coating/steuerung-und-modellierung-der-aggregation-und-redispergierung-gefaellter-nanopartikelsteuerung-und-modellierung-der-aggregation-und-redispergierung-gefaellter-na

29. Brabender DSC25 Extruder [Internet]. [cited 2015 Aug 6]. Available from: http://www.brabender.com/fileadmin/dateien/gb/download/kunststoff/download/broschueren/alle englisch/25055_E_Original_Brabender.pdf

30. Babu padmanabhan. Steer world - extruter times. (Issue 10). Available from: http://extrudertimes.com/ET-website/ET8/index.html#/12/

31. Li Z-M, Li S-N, Yang M-B, Huang R. A novel approach to preparing carbon nanotube reinforced thermoplastic polymer composites. Carbon N Y [Internet]. 2005 Sep [cited 2015 Jan 29];43(11):2413–6. Available from: http://linkinghub.elsevier.com/retrieve/pii/S000862230500237X

32. Opelt C V., Becker D, Lepienski CM, Coelho L a. F. Reinforcement and toughening mechanisms in polymer nanocomposites – Carbon nanotubes and aluminum oxide. Compos Part B Eng [Internet]. Elsevier Ltd; 2015;75:119–26. Available from: http://www.sciencedirect.com/science/article/pii/S1359836815000360

33. Instron UTM [Internet]. [cited 2015 Jul 28]. Available from: http://www.instron.com/en-gb/products/testing-systems/universal-testing-systems/electromechanical/5900/5960-dual-column?region=United Kingdom

34. Kyoung-Yong Chun*a, In-Kyu Moona, Joo-Hee Han*b, Seung-Hoe Dob J-SL and S-YJ. Highly water-soluble multi-walled carbon nanotubes amine-functionalized by supercritical water oxidation †. 2013;(Varian 4100):10171–4.

35. Mombeshora ET, Simoyi R, Nyamori VO, Ndungu PG. Multiwalled Carbon Nanotube-titania Nanocomposites : Understanding Nano-Structural Parameters and Functionality in Dye-sensitized Solar Cells. 2015;153–64.

36. Li L, Li B, Hood M a., Li CY. Carbon nanotube induced polymer crystallization: The formation of nanohybrid shish-kebabs. Polymer (Guildf) [Internet]. Elsevier Ltd; 2009;50(4):953–65. Available from: http://dx.doi.org/10.1016/j.polymer.2008.12.031

37. FEG-SEM Zeiss ULTRAplus, Germany [Internet]. [cited 2015 Aug 27]. Available from: http://matwww.technion.ac.il/Mika/UltraPlus.html

38. Jakob B, Scientific TF, Instruments P. Filter Pressure Value Test (FPV test) - a new standard to examine master batches , white and carbon black colorants. :1–4.

39. Evonik Industries [Internet]. Available from: http://www.plastic-additives.com/product/plastic-additives/en/test-methods/pressure-filter-test/pages/default.aspx

40. EMS-GRIVORY. EMS-CHEMIE HOLDING AG [Internet]. [cited 2016 Jan 1]. Available from: http://kphuaxun.com/cn/grilon/AS_2_E.pdf

41. Bruker ATR FTIR [Internet]. [cited 2015 Aug 1]. Available from: http://wwwchem.uwimona.edu.jm/spectra/JSpecView/iranim/IRmodes/irlab.html

8. ACKNOWLEDGEMENT

Firstly, I would like to thank Professor Andres Krumme, Professor Jaan Kers and Professor Jyrki Vuorinen for providing me such an opportunity to take up this thesis and for trusting in my capabilities to complete the same. Your keen interest in the polymers is truly inspiring and helped me to remain motivated throughout academic field.

I would like express my sincere gratitude to my supervisor Tiia-Maaja Süld and co-supervisor Pasi Keinänen for sharing his knowledge, infinite kindness support, encouragement, helping me in understanding the subject and clarifying in various discussions over the experimental period. All his inputs on approaching the thesis and suggested ideas were vital. Really, I appreciated myself to work under your supervision and look forward for next opportunity.

My special thanks to Triinu Poltimae and Sanna Siljander for exchanging and providing me such a supervisor contact to get this project and introducing me to the other researchers. My sincere thanks to Sukanth Mandal from Prayag Polytech Pvt. Ltd., India, for his help to carry out this research work.

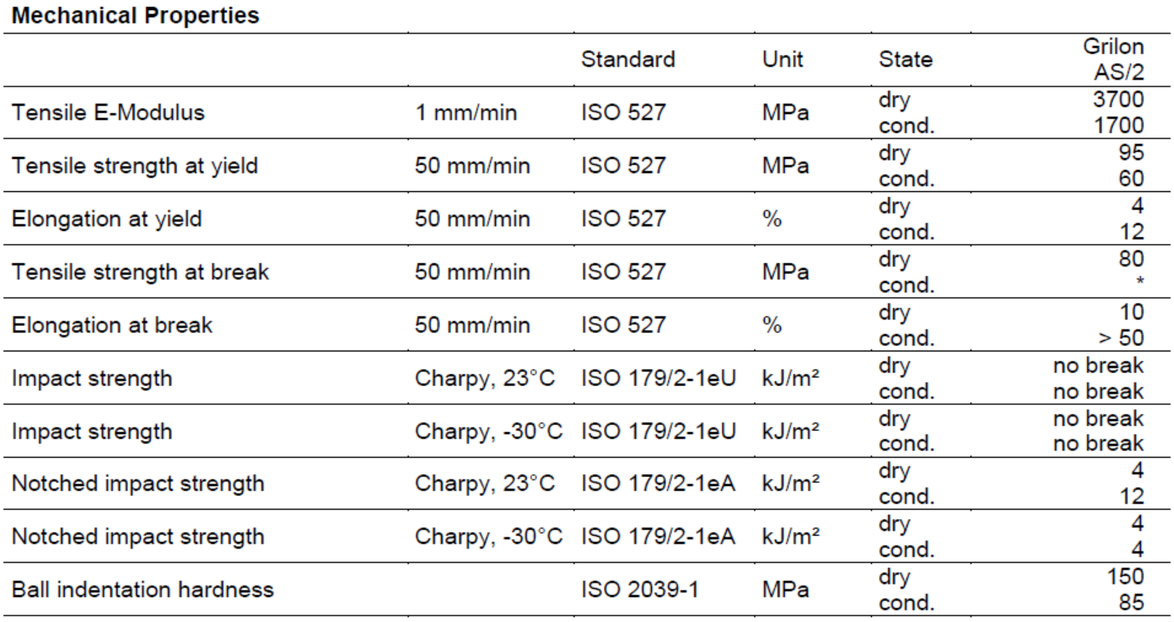
Finally, I take the opportunity to thank my parents, friends and staff that have encourage during my studies.

Tallinn, 18.01.2016

Yashwanth Swamygowda

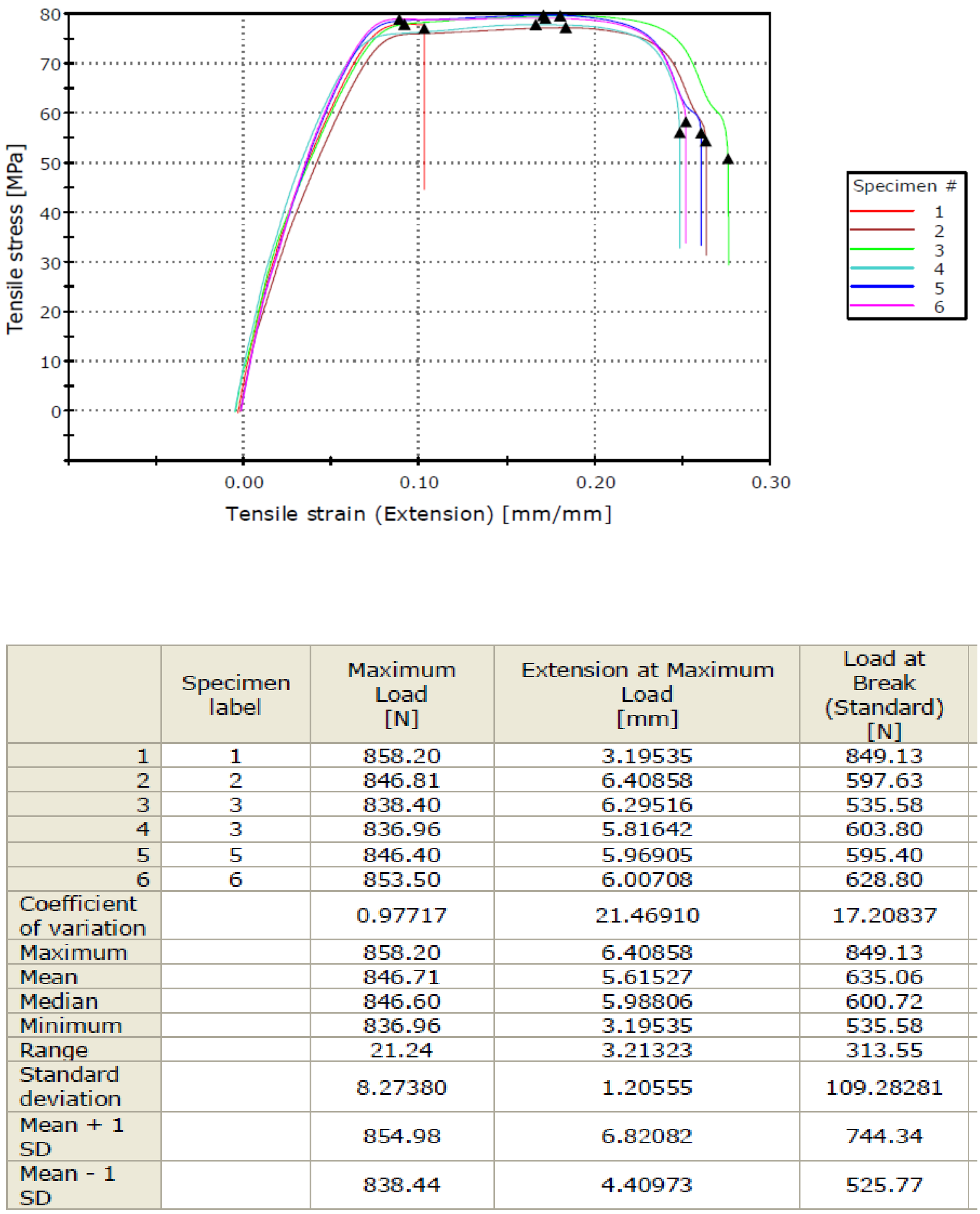
9. APPENDIXES

Table 4. Virgin nylon 66 data obtained from MSDS.[40]



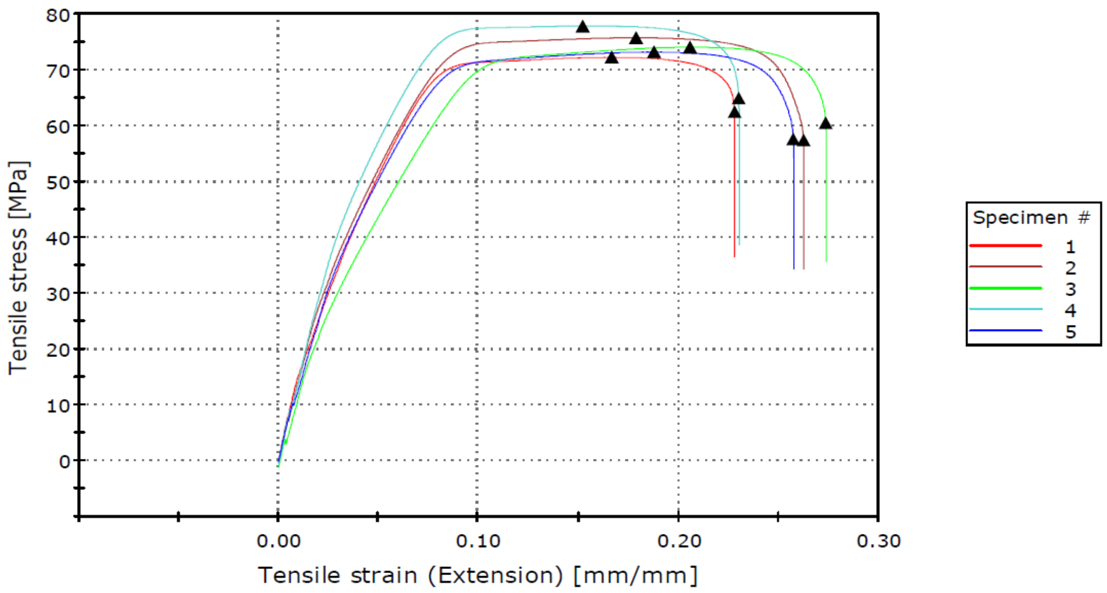
Mechanical Properties

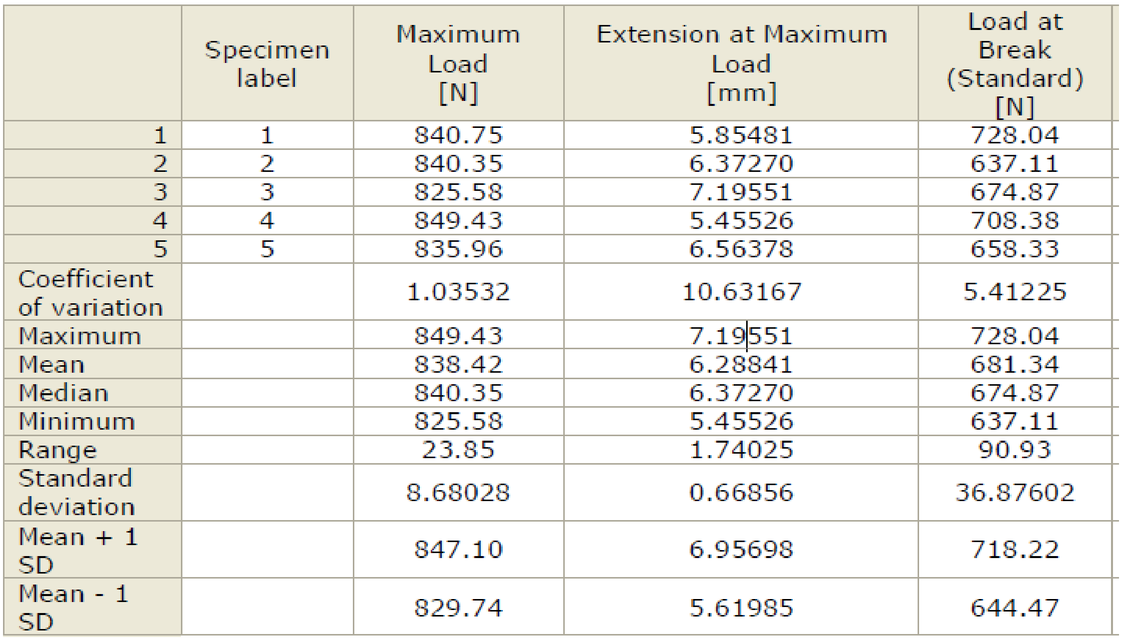
		Standard	Unit	State	Grilon AS/2
Tensile E-Modulus	1 mm/min	ISO 527	MPa	dry cond.	3700 1700
Tensile strength at yield	50 mm/min	ISO 527	MPa	dry cond.	95 60
Elongation at yield	50 mm/min	ISO 527	%	dry cond.	4 12
Tensile strength at break	50 mm/min	ISO 527	MPa	dry cond.	80 *
Elongation at break	50 mm/min	ISO 527	%	dry cond.	10 > 50
Impact strength	Charpy, 23°C	ISO 179/2-1eU	kJ/m²	dry cond.	no break no break
Impact strength	Charpy, -30°C	ISO 179/2-1eU	kJ/m²	dry cond.	no break no break
Notched impact strength	Charpy, 23°C	ISO 179/2-1eA	kJ/m²	dry cond.	4 12
Notched impact strength	Charpy, -30°C	ISO 179/2-1eA	kJ/m²	dry cond.	4 4
Ball indentation hardness		ISO 2039-1	MPa	dry cond.	150 85



	Specimen label	Maximum Load [N]	Extension at Maximum Load [mm]	Load at Break (Standard) [N]
1	1	858.20	3.19535	849.13
2	2	846.81	6.40858	597.63
3	3	838.40	6.29516	535.58
4	3	836.96	5.81642	603.80
5	5	846.40	5.96905	595.40
6	6	853.50	6.00708	628.80
Coefficient of variation		0.97717	21.46910	17.20837
Maximum		858.20	6.40858	849.13
Mean		846.71	5.61527	635.06
Median		846.60	5.98806	600.72
Minimum		836.96	3.19535	535.58
Range		21.24	3.21323	313.55
Standard deviation		8.27380	1.20555	109.28281
Mean + 1 SD		854.98	6.82082	744.34
Mean - 1 SD		838.44	4.40973	525.77

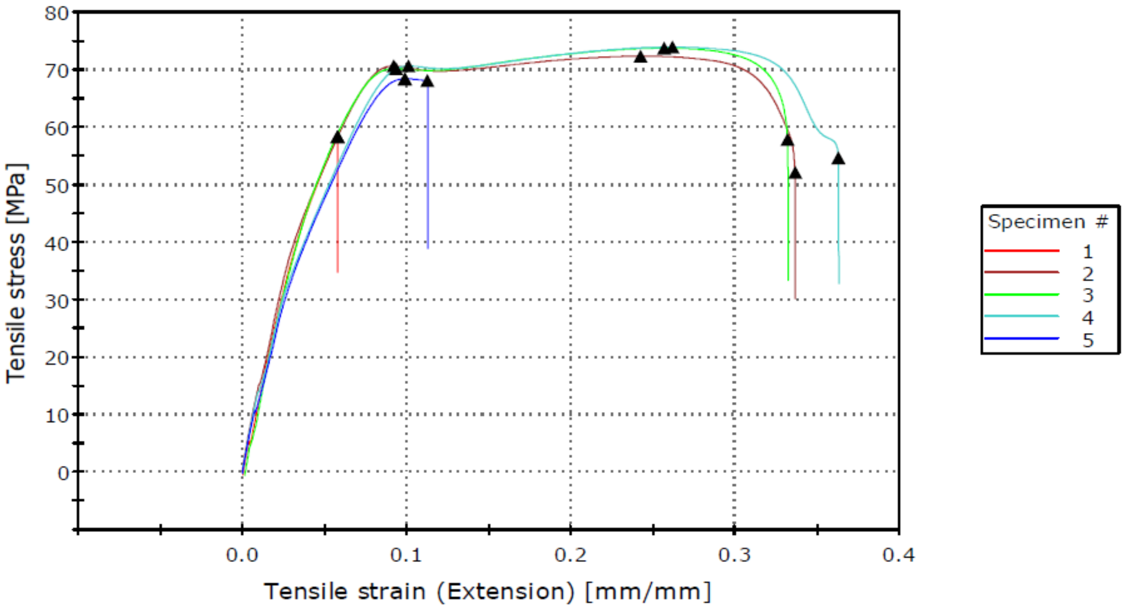
Figure 35. Sample ‘A’ virgin Nylon 66 result generated by software.

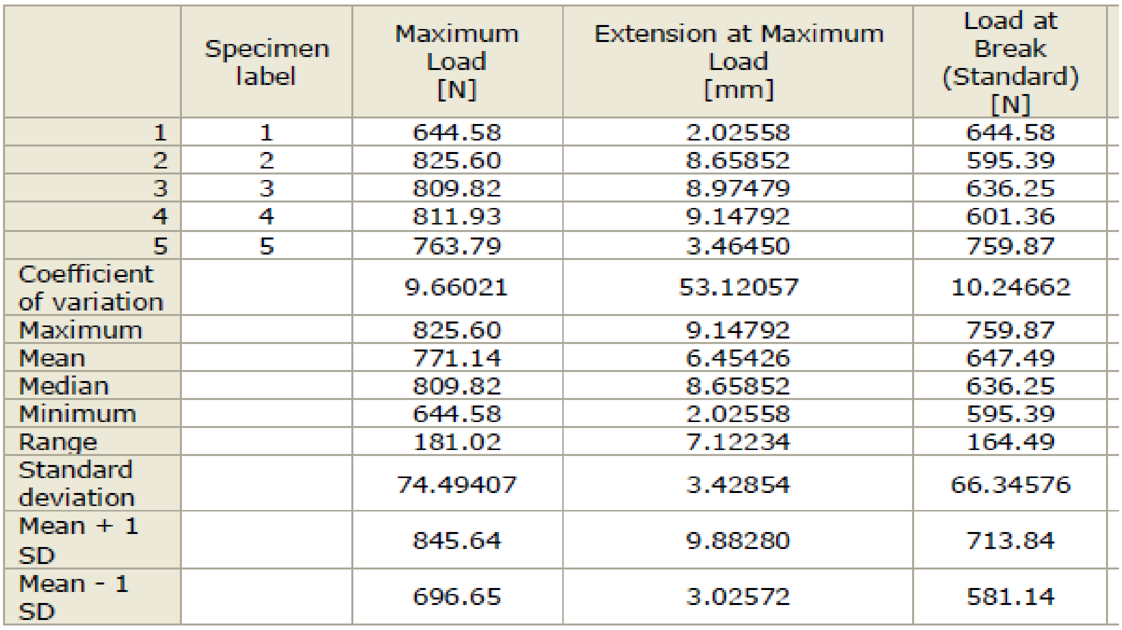




	Specimen label	Maximum Load [N]	Extension at Maximum Load [mm]	Load at Break (Standard) [N]
1	1	840.75	5.85481	728.04
2	2	840.35	6.37270	637.11
3	3	825.58	7.19551	674.87
4	4	849.43	5.45526	708.38
5	5	835.96	6.56378	658.33
Coefficient of variation		1.03532	10.63167	5.41225
Maximum		849.43	7.19551	728.04
Mean		838.42	6.28841	681.34
Median		840.35	6.37270	674.87
Minimum		825.58	5.45526	637.11
Range		23.85	1.74025	90.93
Standard deviation		8.68028	0.66856	36.87602
Mean + 1 SD		847.10	6.95698	718.22
Mean - 1 SD		829.74	5.61985	644.47

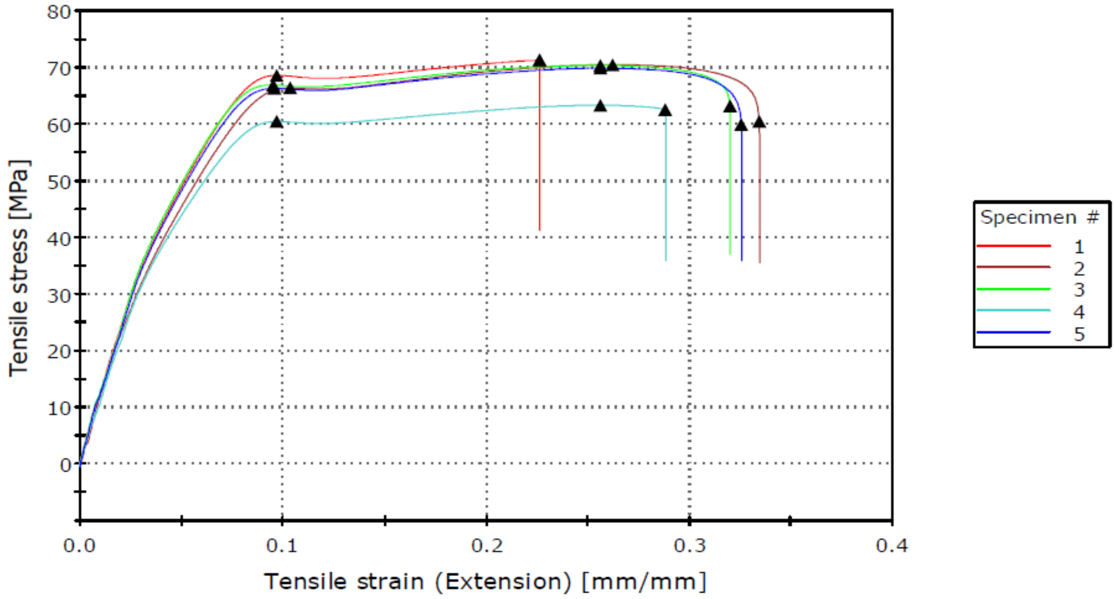
Figure 36. Sample ‘B’ Nylon 66 passed in extruder result generated by software.

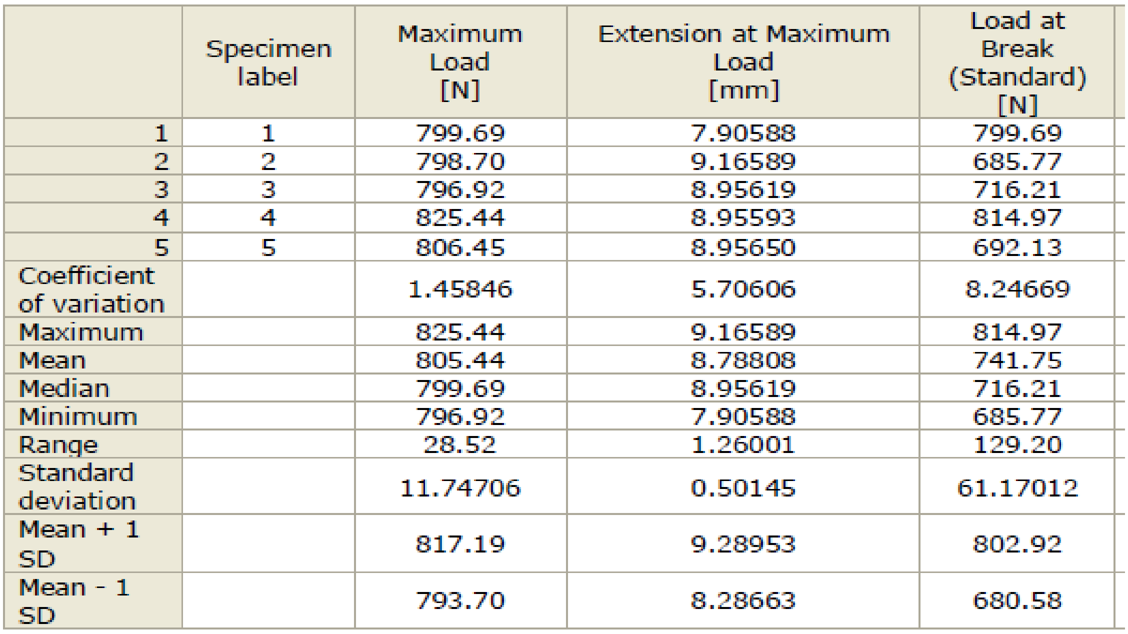




	Specimen label	Maximum Load [N]	Extension at Maximum Load [mm]	Load at Break (Standard) [N]
1	1	644.58	2.02558	644.58
2	2	825.60	8.65852	595.39
3	3	809.82	8.97479	636.25
4	4	811.93	9.14792	601.36
5	5	763.79	3.46450	759.87
Coefficient of variation		9.66021	53.12057	10.24662
Maximum		825.60	9.14792	759.87
Mean		771.14	6.45426	647.49
Median		809.82	8.65852	636.25
Minimum		644.58	2.02558	595.39
Range		181.02	7.12234	164.49
Standard deviation		74.49407	3.42854	66.34576
Mean + 1 SD		845.64	9.88280	713.84
Mean - 1 SD		696.65	3.02572	581.14

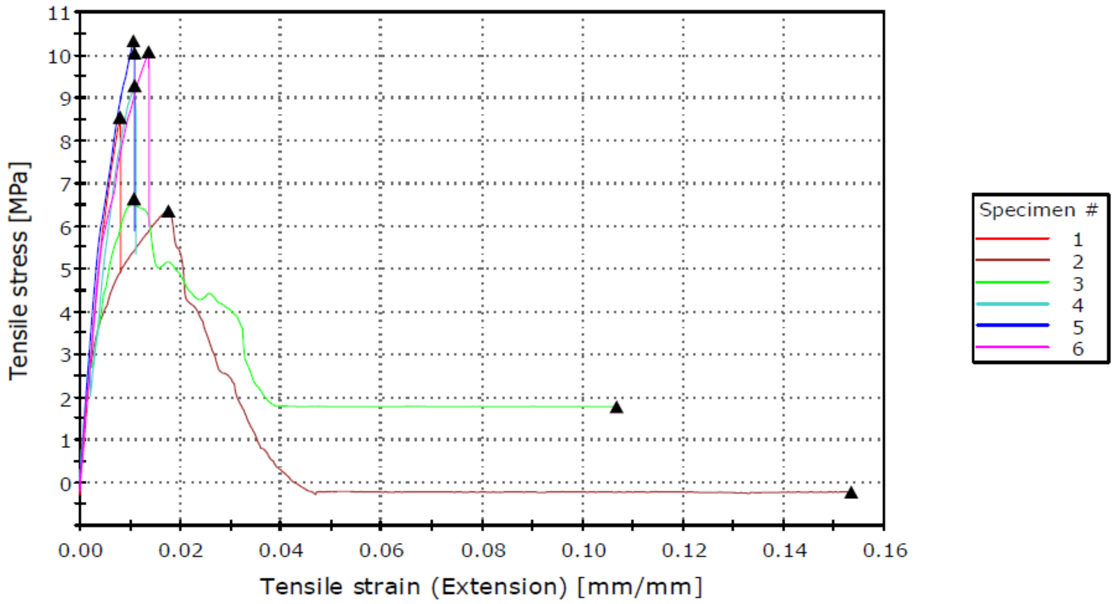
Figure 37. Sample ‘C’ Nylon 66 with pristine CNTs in extruder result generated by software.

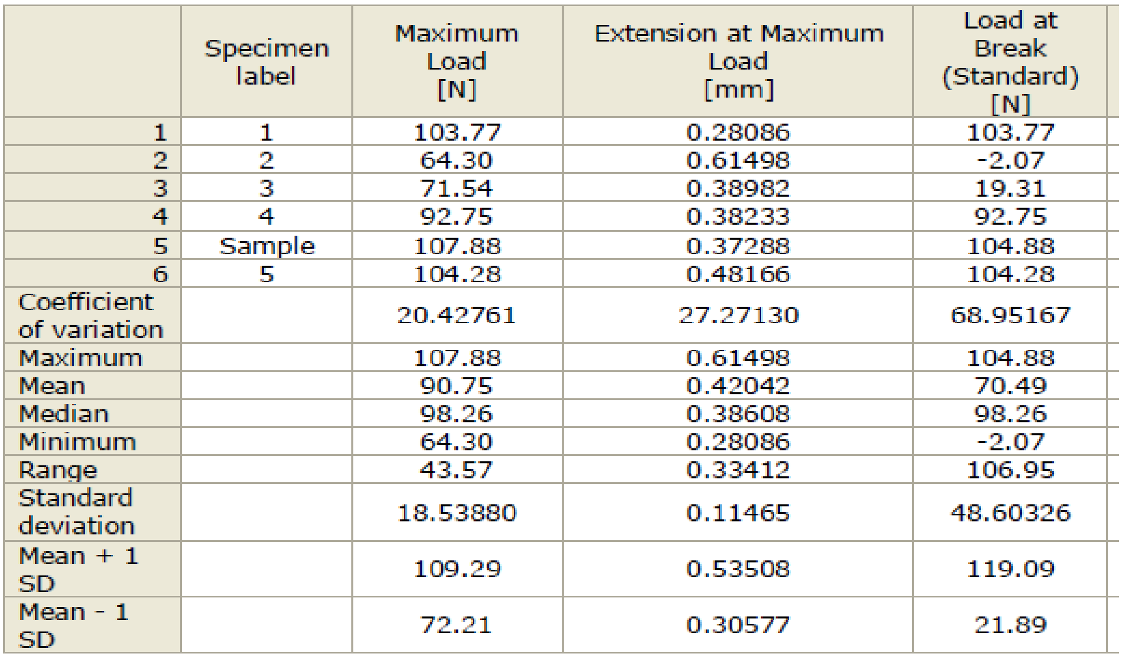




	Specimen label	Maximum Load [N]	Extension at Maximum Load [mm]	Load at Break (Standard) [N]
1	1	799.69	7.90588	799.69
2	2	798.70	9.16589	685.77
3	3	796.92	8.95619	716.21
4	4	825.44	8.95593	814.97
5	5	806.45	8.95650	692.13
Coefficient of variation		1.45846	5.70606	8.24669
Maximum		825.44	9.16589	814.97
Mean		805.44	8.78808	741.75
Median		799.69	8.95619	716.21
Minimum		796.92	7.90588	685.77
Range		28.52	1.26001	129.20
Standard deviation		11.74706	0.50145	61.17012
Mean + 1 SD		817.19	9.28953	802.92
Mean - 1 SD		793.70	8.28663	680.58

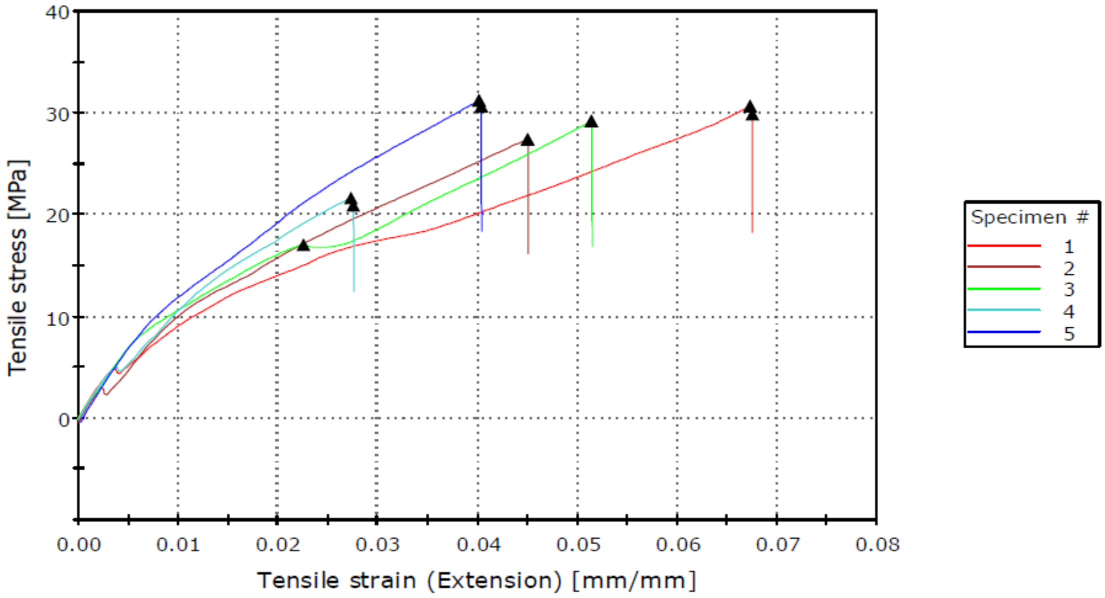
Figure 38. Sample ‘D’ Nylon 66 with water sonicated CNTs in extruder result generated by software.

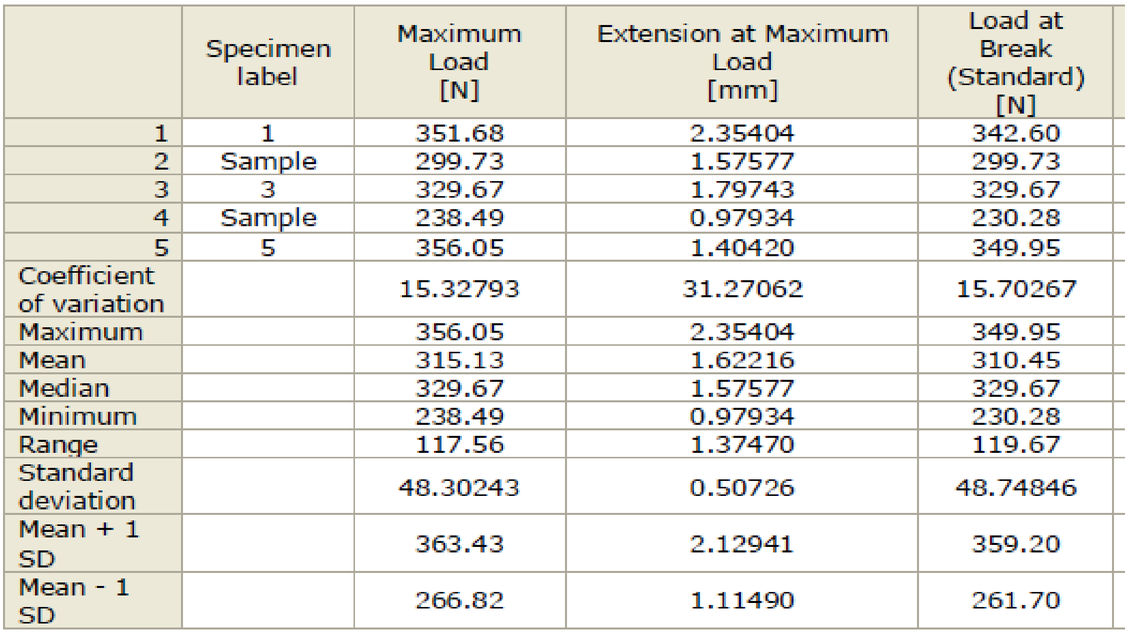




	Specimen label	Maximum Load [N]	Extension at Maximum Load [mm]	Load at Break (Standard) [N]
1	1	103.77	0.28086	103.77
2	2	64.30	0.61498	-2.07
3	3	71.54	0.38982	19.31
4	4	92.75	0.38233	92.75
5	Sample	107.88	0.37288	104.88
6	5	104.28	0.48166	104.28
Coefficient of variation		20.42761	27.27130	68.95167
Maximum		107.88	0.61498	104.88
Mean		90.75	0.42042	70.49
Median		98.26	0.38608	98.26
Minimum		64.30	0.28086	-2.07
Range		43.57	0.33412	106.95
Standard deviation		18.53880	0.11465	48.60326
Mean + 1 SD		109.29	0.53508	119.09
Mean - 1 SD		72.21	0.30577	21.89

Figure 39. Sample ‘E’ Nylon 66 with pristine CNTs in compounder result generated by software.





	Specimen label	Maximum Load [N]	Extension at Maximum Load [mm]	Load at Break (Standard) [N]
1	1	351.68	2.35404	342.60
2	Sample	299.73	1.57577	299.73
3	3	329.67	1.79743	329.67
4	Sample	238.49	0.97934	230.28
5	5	356.05	1.40420	349.95
Coefficient of variation		15.32793	31.27062	15.70267
Maximum		356.05	2.35404	349.95
Mean		315.13	1.62216	310.45
Median		329.67	1.57577	329.67
Minimum		238.49	0.97934	230.28
Range		117.56	1.37470	119.67
Standard deviation		48.30243	0.50726	48.74846
Mean + 1 SD		363.43	2.12941	359.20
Mean - 1 SD		266.82	1.11490	261.70

Figure 40. Sample ‘F’ Nylon 66 with water sonicated CNTs in compounder result generated by software.

Table 5. Tensile test result

Sample	**Extension at maximum load (mm)**	**Load at break (N)**	**Maximum load with stand (N)**
A	6	635	847
B	6	681	832
C	6.45	647	771
D	9	742	805
E	0.42	70	91
F	2	310	315

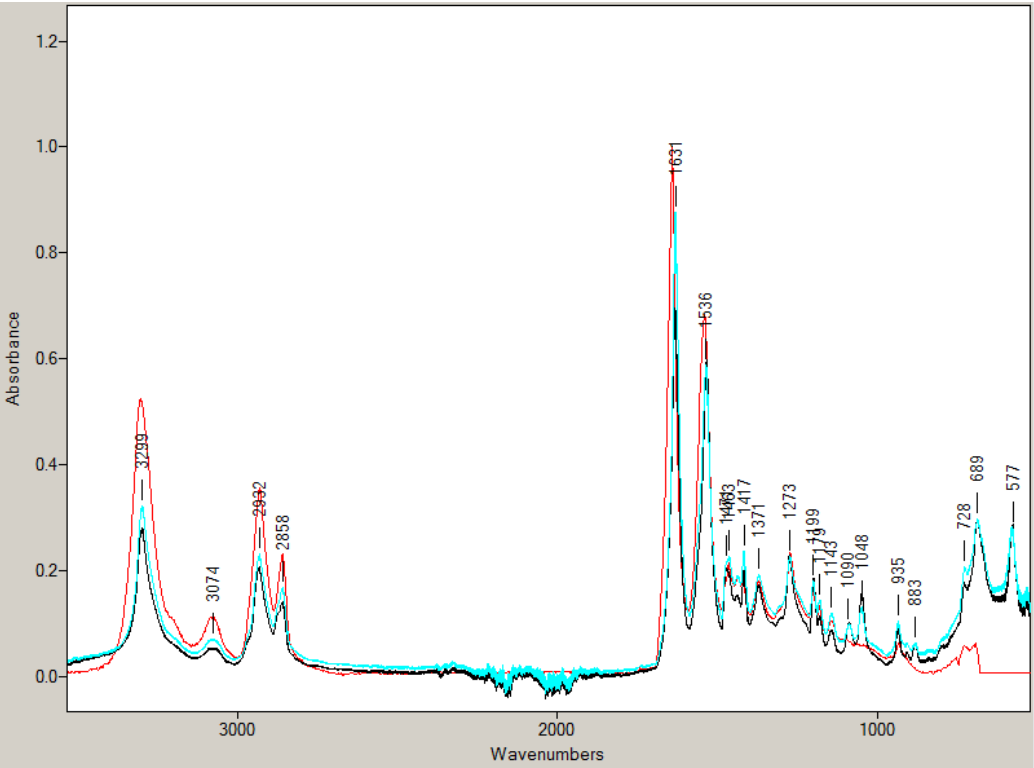


Figure 41. Comparison of sonicated CNTs (blue) and pristine CNT (red)

The above graph is obtained by cross varying with Interspectrum make FTIR instrument - Interspec 200-X using diamond media.

Figure 42. ATR technology functionalized FTIR instrument.[41]

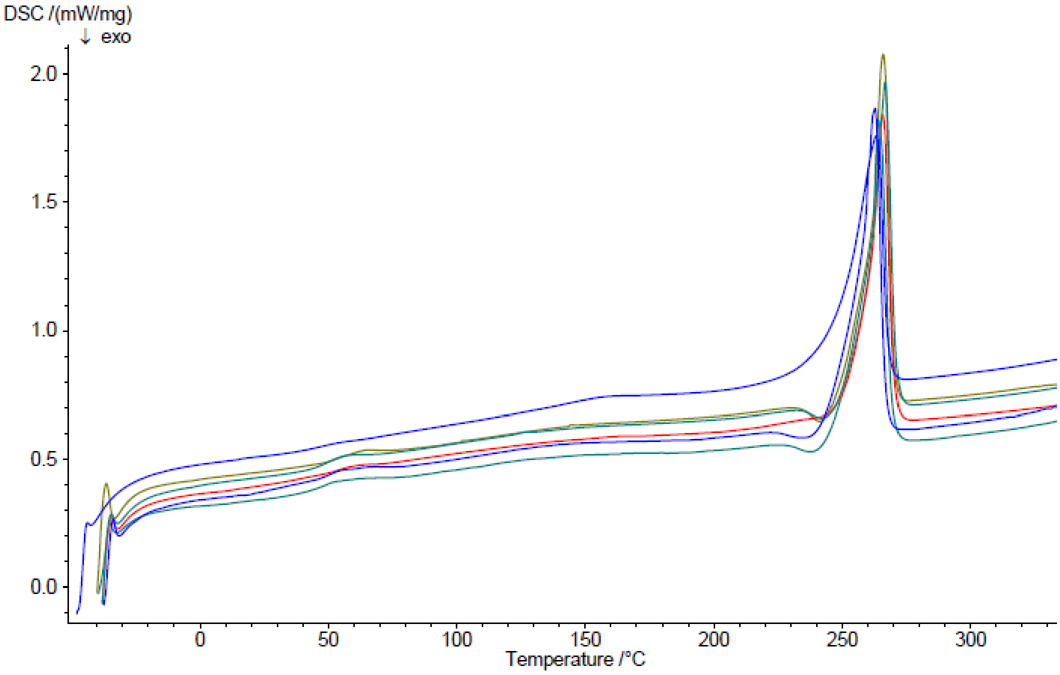


Figure 43. First heating cycle of all samples in DSC.

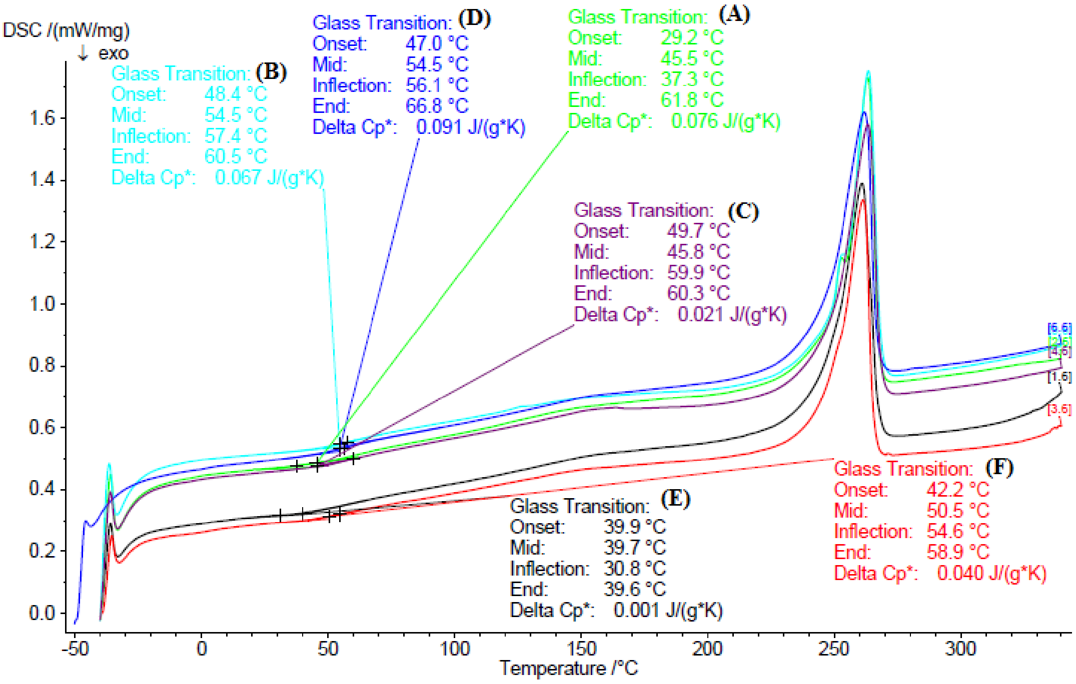


Figure 44. Second heating cycle all samples of DSC with Tg (almost disappeared).

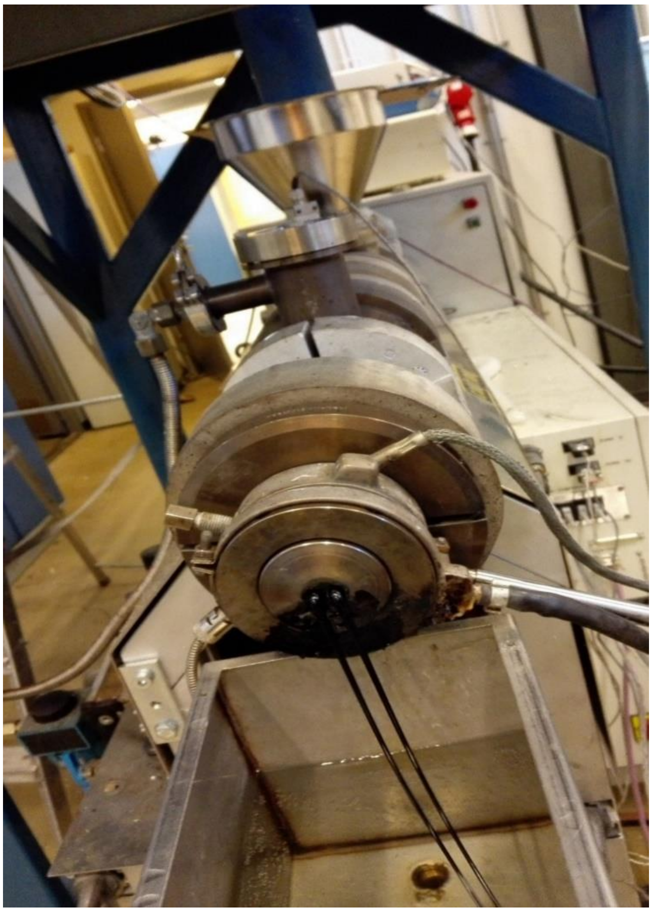


Figure 45. Extruder die head and die hole.

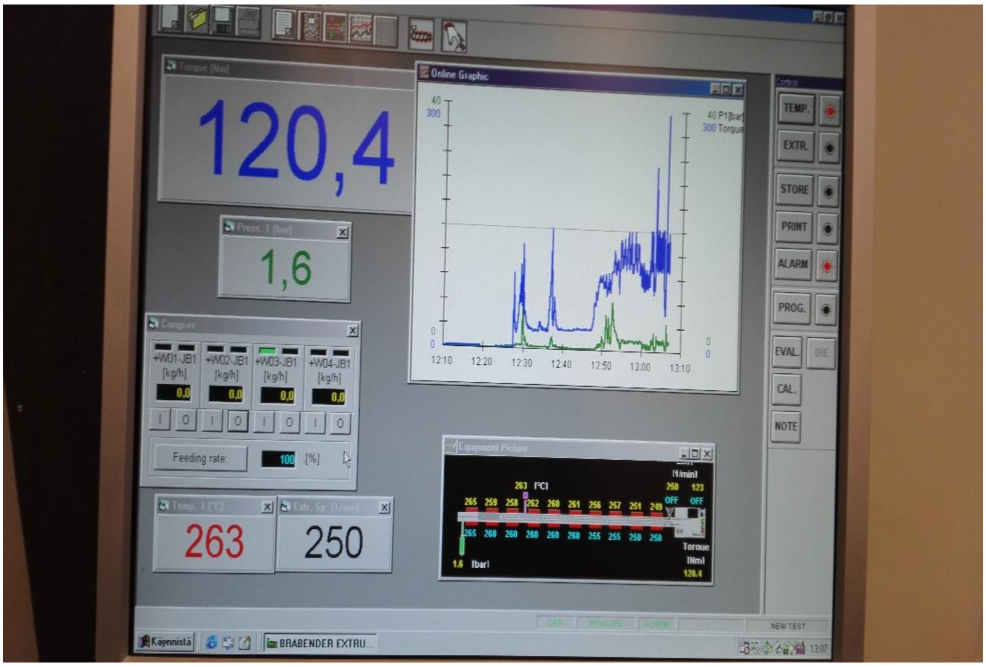


Figure 46. Extruder screen shot during processing - shows torque variation and other parameters to analyze easily.