

# Functionalization and Melt-compounding of MWCNTs in PA-6 for Tribological Applications

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**Abstract.** The present study focuses on the fabrication and mechanical property evaluation of PA-6/MWCNT nanocomposites reinforced with microwave-functionalized MWCNTs. The MWCNTs were subjected to microwave radiation in the solution of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> for 3 minutes, with the aim of achieving better and faster functionalization. The change observed in the crystal structure of PA-6 matrix after CNT addition suggested improved nucleation due to well-dispersed MWCNTs after functionalization. The tensile strength of PA-6 increased by approx. 12 % and 15 % after addition of pristine and functionalized MWCNTs, respectively. This was credited to improved interaction between CNTs and PA-6 matrix. The dispersion quality of CNTs in PA-6 matrix was verified by FEG-SEM, while the fractography of composites revealed polymer sheathing of PA-6 matrix around CNTs. This again contributed in improving the elongation of the composites by approx. 10 %. The wear resistance of the composites also improved appreciably, irrespective of the applied load. The specific wear rate of PA-6/CNT nanocomposite reinforced with functionalized MWCNTs increased by approx. 60 to 70 %, while coefficient of friction reduced by approx. 30 to 40%.

**Keywords:** Microwave functionalization; Melt compounding; PA-6/MWCNT nanocomposite; Polymer sheathing; Sliding Wear.

## 1. Introduction

Polymer/CNT nanocomposites are accelerating its importance in actual applications due to their exceptional set of properties such as high strength, improved stiffness, better thermal and electrical conductivity, enhanced wear performance, etc. [1-3]. Nylon-6 (PA-6) is a well known bearing and gear material owing to its high wear resistance [4,5]. It is also used in automobiles for sliding components of fuel tank, door assemblies, structural and load bearing parts, etc. [6]. But further improvement is still desired for more demanding applications.

PA-6 polymeric parts, though being used in areas where temperatures are not too high and are subjected to lesser loads than their metallic counterparts, are still prone to continuous wear and tear. This gives rise to problems related to the strength of materials, performance of the components, safety and life of the part. Hence, the elements in such cases are expected to have better properties than virgin polymers. Previous literature has shown significant improvement in the mechanical properties of PA-6 on the addition of MWCNTs.

Liu et. al. [7] reported homogenous dispersion of CNTs throughout PA-6 matrix when incorporated in 0.5, 1 and 2 wt.%. They noted a 214% rise in elastic modulus and 162% increase in yield strength, but 26% decrease was reported in tensile strength. This indicated brittleness of matrix after CNT addition. The



authors also reported increase in crystallinity of the PA-6 composites. Meng et. al. [5] studied the mechanical properties and crystallization behavior of PA-6/CNT composites with 1% CNT addition. The authors reported an increase in the tensile strength, Young's modulus and microhardness of PA-6/CNT composite which was attributed to well dispersed CNTs and improved load carrying capacity of the matrix. The composites exhibited a lower value of friction coefficient and higher wear resistance which is due to the fact that CNTs acts as solid lubricants to reduce friction.

The efficient utilization of CNTs mainly depends on its dispersion throughout the matrix. The strong van der Waals' force of attraction between CNT surfaces causes them to agglomerate and consequently deteriorate the properties of nanocomposites. Thus, despite of high surface area the nanotubes behave like stress concentration points, leading to excessive agglomeration behaviour [8]. Thus, to overcome this difficulty functionalization of CNTs is a potential route. The homogeneous dispersion of filler within the matrix is important for composite properties. Also, stabilization of the dispersion is vital in order to prevent re-aggregation [8]. Functionalization enhances the properties of composites and, thus, consequently their application potential.

There are many effective methods to functionalize CNTs such as covalent modification or non-covalent approaches including polymer wrapping, bio-molecule binding and metal ion binding [9,10]. Other functionalization routes which have been thought to make them chemically active in the past few years, include chemical and solid-phase or hydro-mechano-chemical method [10]. Sonication and shear mixing are generally used to disperse CNTs but these techniques do not give reproducible and durable results. On the other hand, chemical functionalization can help stabilizing the dispersion and allow coupling them with a polymer matrix. This improves the adhesion between the CNTs and the polymer matrix, so that the external stress can be efficiently transferred to the nanotubes [8].

Despite achieving the improvement in dispersion quality of CNTs, the harsh environment of acids during long hours of sonication and/or refluxing causes damage to the CNTs. The damage so caused affects the structural integrity of CNTs, wherein the purpose of functionalization is lost. Thus, improved as well as less damaging routes for functionalization of CNTs are needed. The microwave treatment of CNTs is steadily emerging as a novel, faster and more efficient technique to achieve functionalization of CNTs, [11, 12], moreover in an eco-friendly way.

The review of previous literature indicates that the effect of using microwave-functionalized MWCNT as reinforcement on the tribological properties of PA-6 has gained little attention, to the best of our knowledge. Thus, the present paper focuses on exploring the tribological performance of PA-6 reinforced with non-functionalized as well as microwave-functionalized MWCNTs. This will aid in understanding the polymeric systems that are actually used for heavy duty applications demanding high strength and wear resistance.

## **2. Materials and methods**

### **2.1. Materials**

PA-6 in the form of granules, Grade: Gujlon M28RC (density: 1.13 g/cm<sup>3</sup>), was procured from GSFC, Gujarat. MWCNTs with purity >98% were procured from AdNano Technologies Pvt. Ltd. with mean outer diameter 20-30 nm, mean inner diameter 10-20 nm and mean length of 20-30  $\mu$ m. The chemicals used for functionalization were nitric acid (purity~69%) and sulphuric acid (purity~98%), obtained from Loba Chemie.

### **2.2. Functionalization**

For microwave-functionalization; the as-received MWCNTs were added to 1:1 solution of HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> and subjected to microwave exposure (at 50% capacity of 700W) for 3 minutes. The MWCNTs were then washed with DI water until neutral pH was obtained and later dried at 80°C for 2 hours. The non-functionalized and microwave-functionalized MWCNTs were then mixed with PA-6

granules in fixed proportion of 0.5 wt. % by melt-compounding technique. The codes assigned to the different samples for this study is given in **Table 1**.

**Table 1** Sample coding for polymer and its composites under study

Composition	Sample Code
Virgin PA-6	V-PA
PA-6 + 0.5 wt.% non-functionalized MWCNT	PA/CNT
PA-6 + 0.5 wt.% microwave-functionalized MWCNT	PA/f-CNT

### 2.3. Characterization

The dispersion quality of the non-functionalized and microwave-functionalized MWCNTs in PA-6 matrix was investigated by analyzing the cryo-fractured surface of melt-compounded sample using a Field Emission Scanning Electron Microscope (Make: JEOL, Model: JSM-7610F) at different magnifications. The X-ray diffraction patterns for nanocomposites under study were generated on XRD machine (Make: PAN-alytical, Model: X'Pert Pro) from 10° to 100° 2 $\theta$  positions, with 0.01° scan step size and 20 sec time per step.

### 2.4. Tensile testing

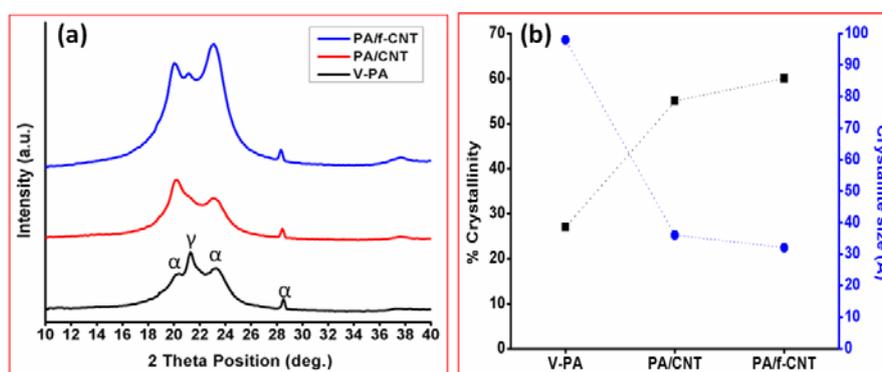
The Type-I dumbbell shaped samples (according to ASTM standard D638) were used for tensile testing. The tensile properties of the samples were determined according to ASTM Standard D638 using a universal testing machine (Make: INSTRON, Model: 4467) at a crosshead speed of 5 mm/min. Five test results were averaged and then reported in this study. The morphology of the tensile fractured surfaces of the samples was investigated by Field Emission Scanning Electron Microscope (Make: JEOL, Model: JSM-7610F) at different magnifications.

### 2.5. Wear testing

The wear performance of both the virgin PA-6 and the PA-6/MWCNT nanocomposites was evaluated on a pin-on-disc Wear and Friction monitor (Make: DUCOM, Model: TR-20LEMI). The samples with dimension 10 mm x 10 mm x 30 mm were tested under 20, 60 and 100 N of loads. The surface was first abraded with superfine SiC paper (grade 1500) for uniform contact, cleaned with acetone, dried and weighed prior to experimentation. The pin was then continuously abraded for 3 minutes against the SiC paper (grade 220) as counter-face at a speed of 200 RPM and track diameter of 80 mm. Three test results were averaged for each type of sample and then reported in this study. The worn out surfaces of the samples were investigated by scanning electron microscope (Make: SEM-JEOL, Model: 6380A).

## 3. Results and discussion

The change in crystal structure of PA-6 after reinforcing non-functionalized and microwave-functionalized MWCNTs was evaluated with the help of XRD. **Fig. 1** shows the XRD diffractogram for V-PA, PA/CNT and PA/f-CNT samples.

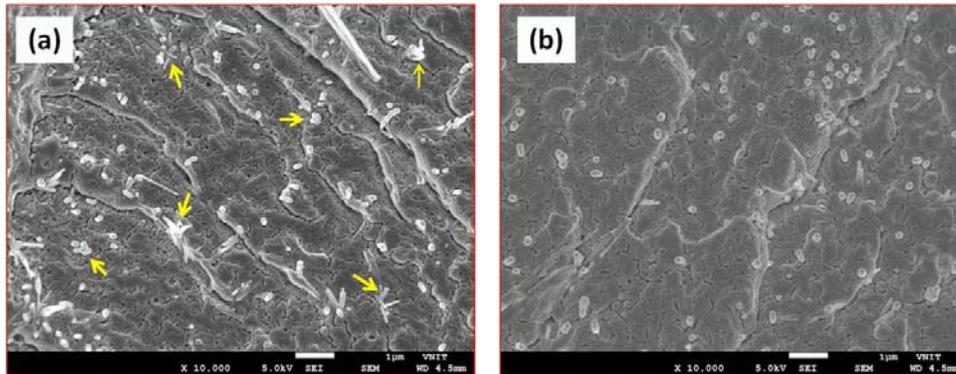


**Fig. 1(a)** XRD diffractograms for PA-6 and PA-6/MWCNT nanocomposites; **(b)** % crystallinity vs. crystallite size data

**Fig. 1(a)** depicts the XRD diffractograms of the samples under study. For virgin PA-6; prominent diffraction peaks observed at  $2\theta$  positions of  $20.13^\circ$ ,  $23.44^\circ$  and  $28.52^\circ$  corresponds to  $\alpha$ -phase and that at  $21.22^\circ$  position corresponds to  $\gamma$ -phase, both monoclinic in structure. These peaks are the reflections from (200), (002,220), (210) and (100,010) planes respectively [7,13,14]. The  $\alpha$ -phase of PA-6 is a more thermally stable phase consisting of sheets of hydrogen-bonded chains that are packed in an anti-parallel fashion, whereas the  $\gamma$ -phase is the less stable phase formed due to random hydrogen bonding between parallel chains [4,14]. The characteristic peaks for  $\alpha$ -phase were observed in PA-6/MWCNT nanocomposites also, but the peak for  $\gamma$ -phase disappeared in case of PA/CNT sample, but was present for PA/f-CNT composite. However, the intensity of this  $\gamma$ -phase peak in PA/f-CNT nanocomposite was comparatively lower than that of virgin PA-6. The reduction or disappearance of  $\gamma$ -phase peak indicates the fact that addition of CNTs changes the crystal structure of PA-6 matrix from *partial- $\alpha$ /partial- $\gamma$*  into *complete  $\alpha$ -structure*, also reported previously [4,7,13]. An increase in the intensity of  $\alpha$ -structure phase indicates more volume fraction of stable and crystalline polymeric phases present in the matrix. This hints towards improved nucleation, as evident from the reduced crystallite size ( $C$ ) and increased % crystallinity (%  $X_c$ ) shown in **Fig. 1(b)**. The change in % crystallinity and crystallite size of PA-6/MWCNT nanocomposites points out towards the fact that MWCNT act as effective heterogeneous nucleating agents for PA-6 matrix [4,8,13]. The long fibrillar structure of CNTs provide ideal nucleation sites for polymer chains to tether and the crystal growth becomes easier [5,14,15], thus promoting crystallization of polymer matrix.

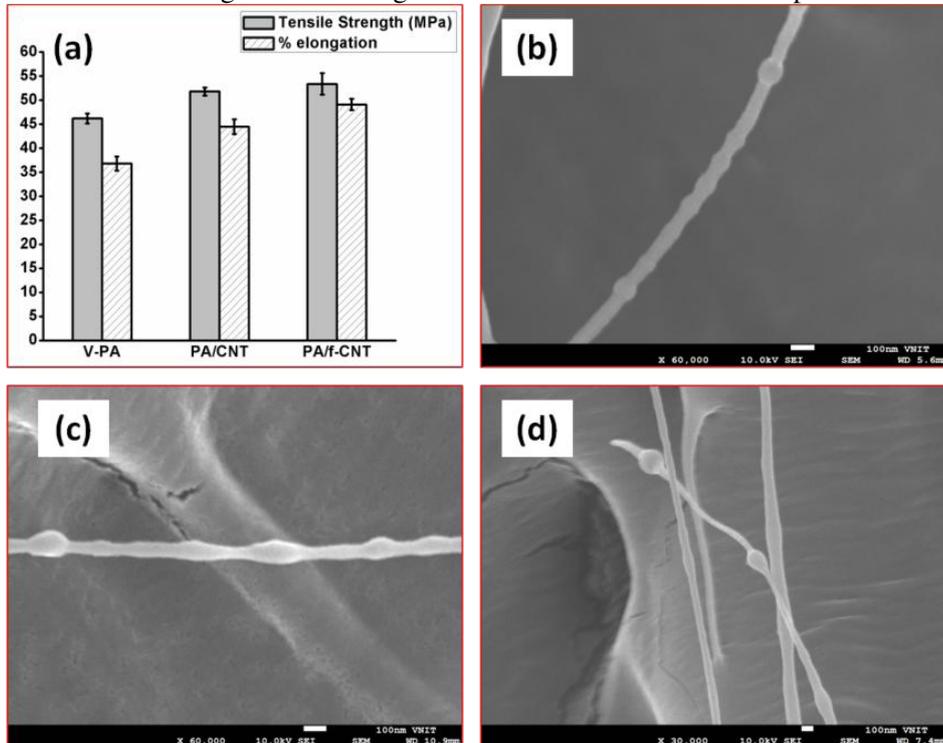
The dispersion of non-functionalized and microwave-functionalized MWCNTs within PA-6 matrix was investigated by electron microscopy of cryo-fractured composite surfaces. **Fig. 2** shows the SEM micrographs of PA/CNT and PA/f-CNT samples.

It is evident from the micrographs that the non-functionalized as well microwave-functionalized MWCNTs were well-dispersed throughout the PA-6 matrix. As seen from **Fig. 2(a)**; the non-functionalized MWCNTs were found in bundles in some places, as indicated by arrows. Apart from the few bundled MWCNTs, there was no indication of significant agglomerate formation PA/CNT samples. On the other hand, it can be easily inferred from **Fig. 2(b)** that the microwave-functionalized MWCNTs were uniformly distributed across PA-6 matrix, with no CNT bundles or agglomerates. This can be credited to the attachment of polar functional group  $-\text{COOH}$  on the surface of MWCNT. The strong opposing polarity of  $-\text{COOH}$  functional groups allow the individual nanotubes to repel each other and hence, avoid agglomeration within polymer melt. Furthermore, the mixing force incorporated during melt-compounding again makes the agglomeration of CNTs difficult physically, therefore leading to improved dispersion quality.



**Fig. 2** SEM micrographs of PA-6 and PA-6/MWCNT nanocomposites

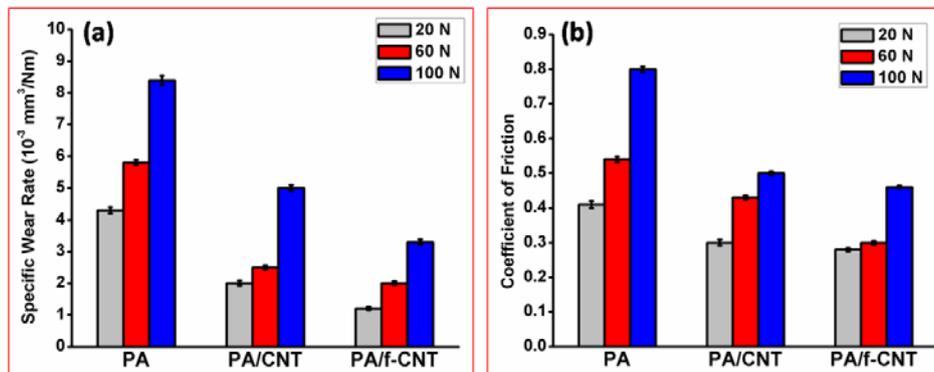
**Fig. 3(a)** depicts the tensile strength and % elongation of PA-6/MWCNT nanocomposites under study.



**Fig. 3(a)** Tensile strength and % elongation of PA-6 and PA-6/MWCNT nanocomposites; Polymer sheathing in **(b)** PA/CNT and **(c)** PA/f-CNT; **(d)** MWCNTs bridging across matrix

It is evident from the figure that the tensile properties of the PA-6 nanocomposites increased. The tensile strength of PA-6 increased by approx. 12 % and 15 % after addition of non-functionalized and microwave-functionalized MWCNTs, respectively. This can be attributed to the improved interaction between well-dispersed MWCNTs and PA-6 matrix, as evident from the fractograph shown in **Fig. 3(b)-(c)**. The figure reveals polymer sheathing of PA-6 matrix around the MWCNTs. This polymer sheathing layer plays a significant role in effective load transfer and hence advocates for the increase in tensile strength PA-6/MWCNT nanocomposites under study. **Fig. 3(d)** shows multiple MWCNTs bridged across fractured PA-6 matrix. These MWCNTs were fully stretched across the broken matrix due to the deformation during fracture [7,16,17]. This again contributes in improving the elongation of the nanocomposites by approx. 10 %.

The wear performance of the PA-6 and PA-6/MWCNT nanocomposites was evaluated in terms of the specific wear rate (SWR) and coefficient of friction (CoF), as shown in **Fig. 4**.

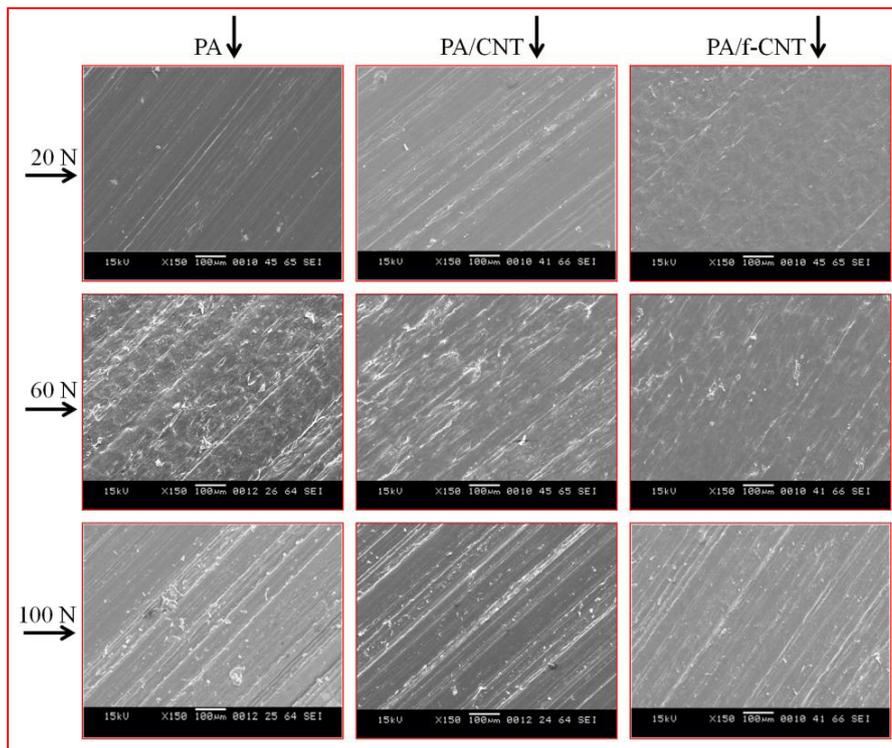


**Fig. 4(a)** Specific wear rate and **(b)** Coefficient of Friction of PA-6 and PA-6/MWCNT nanocomposites

As evident from **Fig. 4(a)**, the specific wear rate of PA-6 reduced after CNT addition, irrespective of the applied load. At 20 N load; the SWR of PA/CNT and PA/f-CNT reduced by approx. 53% and 72%, respectively. At 60 N load; the SWR reduced by approx. 56% and 65%, while at 100 N load; it reduced by approx. 40% and 60% for PA/CNT and PA/f-CNT, respectively. It is, thus, clear here that decrease in the wear rate was more in case of PA-6 reinforced with microwave-functionalized MWCNTs. This can be attributed to the fact that the functionalized CNTs are well-dispersed throughout the matrix which enhances the load carrying capacity of the composite [5,18]. The well-dispersed CNTs anchor firmly within the PA-6 matrix, thus, making the removal of material from the surface more difficult. This, in turn, led to the improvement in wear resistance of the material. However, it can also be seen from **Fig. 4(a)** that as the applied load increases, the SWR of the sample also increases significantly. This agrees well with the fact that wear loss is directly proportional to load, as reported by others also [5,18,19,20].

The variation in the coefficient of friction of PA-6 and PA-6/MWCNT nanocomposites, shown in **Fig. 4(b)**, is similar to that of the specific wear rate. The lowest CoF was observed for PA/f-CNT sample, irrespective of the applied load. But the coefficient increased with increasing applied load for all the samples. The CoF for PA/CNT reduced by approx. 26%, 20% and 37% at 20N, 60N and 100N load, respectively, while that for PA/f-CNT it reduced by 31%, 44% and 42%. The lower CoF in case of PA/f-CNT indicates the fact that improved dispersion increases the surface area of CNTs for contact during sliding, thus, reducing direct contact between the counter-face and the composite surface [5,18,21,22]. This also confirms that the CNTs act as solid lubricants during the sliding wear of PA-6 and initiates self-lubricating action when exposed to the hard counter-face [18,22].

The worn-out surfaces of PA-6 and PA-6/MWCNT nanocomposites tested for wear performance at different loads are shown in **Fig. 5**. The SEM micrographs are taken at 150x magnification with scale bar of 100 $\mu$ m.



**Fig. 5** Worn-out surfaces of PA-6 and PA-6/MWCNT nanocomposites at different loads

It is clear from **Fig. 5** that, irrespective of load; the worn-out surfaces of virgin PA-6 showed more peeling and ploughing as compared to the nanocomposites, which indicates that adhesive and ploughing wear mechanisms are dominant [5]. The relatively smoother surface seen for PA/f-CNT samples agrees well with the specific wear rate and coefficient of friction of also. Thus, confirming the claim that microwave-functionalized CNTs help to improve the properties of the PA-6 matrix by intercalating with the polymer chains [23] and thereby enhancing the load carrying capacity of PA-6 during tensile as well as tribological loading. In addition, it can be seen here that the wear tracks on PA-6 surfaces are thicker and deeper as compared to the nanocomposites. This can be credited to the nano-reinforcing effect of the CNTs that hold down the matrix material during loading [24]. Furthermore, the CNTs that are released during continuous sliding get transferred to the contact area between sample surface and counter-face. These CNTs then could serve as solid lubricants and further prevent direct contact between sliding surfaces, thereby improving the wear resistance of the composites [5]. Thus, it can be inferred here that introducing CNTs into the PA-6 matrix suppresses the wear of the composite's surface successfully.

#### 4. Conclusion

A systematic investigation on the mechanical properties of MWCNT reinforced PA-6 was successfully carried out. The nano-reinforcing effect and better load carrying capacity of microwave-functionalized MWCNTs gave superior tensile strength to the composites, while enhanced wetting at the interphase improved elongation. Also, the self-lubrication action of CNTs enhanced the wear resistance of the surface by making removal of material more difficult. This helped to suppress the adhesion and ploughing wear in composites, which was otherwise dominant in virgin PA-6. Thus, this study advocates the addition of microwave-functionalized MWCNTs into PA-6 matrix to be beneficial from application point-of-view.

## 5. References

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