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## Investigating mechanical and thermal properties of polypropylene/carbon nanotubes composites --Manuscript Draft--

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<b>Abstract:</b>	Multi-walled carbon nanotube-polypropylene nano-composite loaded at 0.01 to 5wt% of CNTs has been prepared using twin-screw mixer. The rheological and thermo-mechanical properties have been studied using rheometer and tensile machine. The CNTs were well dispersed in PP with fairly good dispersion stability. The effect of the volume fraction of CNT reinforcements on the Young's modulus of the nano-composites is investigated.

# Investigating mechanical and thermal properties of polypropylene/carbon nanotubes composites

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## Abstract.

Multi-walled carbon nanotube-polypropylene nano-composite loaded at 0.01 to 5wt% of CNTs has been prepared using twin-screw mixer. The rheological and thermo-mechanical properties have been studied using rheometer and tensile machine. The CNTs were well dispersed in PP with fairly good dispersion stability. The effect of the volume fraction of CNT reinforcements on the Young's modulus of the nano-composites is investigated.

**Keywords:** Nano-composite material, dispersion, rheology, mechanical properties.

## 1. Introduction

For the last decade CNTs have been considered as promising nano-sized reinforcing fillers with a random orientation similar to conventional short fiber reinforced composites. In fact, the outstanding thermo-mechanical and electrical properties of these carbon nanotubes (CNTs) have made them among the most promising materials in a wide range of applications [1-3].

However, the incorporation of CNTs in a polymer or ceramic matrix does not result in an outstanding improvement of the corresponding properties of the composite. One of the most difficult problem concerning nanocarbon-filled composites is associated with the dispersion of carbon nanotubes or other nanoparticles into a polymer matrix [6-9]. Good dispersion and intimate contact between the filler and the matrix are major challenges to fully realize outstanding properties of CNTs in composite materials. The nature of the polymer binder also plays an important role in the formation of a composite properties complex. In addition, the twin-screw mixer technique is widely used for incorporation of nano-carbons in highly viscous melts. It's well suited to overcome some of these problems associated with the dispersion of CNTs. This approach allows using moderate shear rates and shear stress, making viscous polymer blends relatively easy to process. Shear stress arises from the screw rotations that provide better dispersion of particle in polymer matrix. Although some experiments have been conducted on material properties of CNT reinforced composites scattered data on the nano-reinforced composites have been reported in

literature [10-14]. The main reasons for the inconsistency are attributed to drawbacks in the uniform alignment of CNT reinforcements and forming proper interfacial bonding between matrix and CNTs during the mixing process of the composites. Prashantha et al. [15] report on PP-CNTs nanocomposites produced with varying CNTs content by diluting a commercial masterbatch in a twin screw extruder. They show that CNTs enhance tensile modulus and yield stress, while reducing the ductility of nanocomposites systems. Flexural properties increases with CNTs content with maximum benefits observed for 2wt% CNTs filled nanocomposites. Szentes et al. [16] compare PP nanocomposites filled with CNTs prepared by single crew extruder and twin screw extruder. By increasing the CNTs content up to 5wt%, the value of nanocomposites melt flow rate decreases more for samples obtained by twin screw extruder as a sign of a better homogeneity achieved with process. Xu and Wang [17] showed that the formation of the CNTs network could mainly restrict the mobility and diffusion of PP chains to crystal growth fronts. Typically, CNTs are considered to be nucleation agents that accelerate PP crystallization, while CNTs networks can impose physical confinement on polymer crystal growth. Frankland et al. [18] investigated stress-strain curves of single-walled CNTs reinforced polyethylene matrix composites. They reported that long SWCNTs enhance the stiffness of nanocomposites obviously; however, no significant enhancement was observed for short SWCNTs. Zhao and coworkers [19] report substantial increase of tensile modulus and strength by adding small amounts of CNTs to a PP matrix in a co-rotating twin screw extruder.

The aim of this work is to improve mechanical and thermal performance of polypropylene by addition of carbon nanotubes (CNTs). Tensile strength, elastic modulus and elongation at break have been determined from tensile tests and thermal degradation has been followed by thermogravimetric analysis (TGA). In particular, degradation temperature at 0.01wt% and 5wt% weight loss has been determined as a representative parameter of the degradation improvement.

## **2. Experimental Methods**

### **2.1. Materials**

The multi-walled carbon nanotubes (NC7000) produced by chemical vapor deposition (CVD) were purchased from Nanocyl Company® (Belgium). The mean diameter of the MWNTs was about 15-30 nm with the purity of 90%.

The polymer matrix used to elaborate the nano-composites was a semi-crystalline thermoplastic polypropylene (PP-EP548N) produced by Sabic Company<sup>®</sup> with melt flow Index (MFI) = 11g/10min (230 °C/2.16 kg) and density = 0.892g/mm<sup>3</sup>.

## **2.2. Preparation of nano-composites**

The thermoplastic polypropylene was introduced in the a Brabender<sup>®</sup> mixer with a pair of rotor blades. Then, CNTs were then introduced, after the melting of the thermoplastic matrix. For the melt mixing process, the rotation speed and temperature of the mixing chamber were set at 30 rpm and 180 °C, respectively, and the blending continued for 30 min. The CNTs concentration was varied as 0 to 5 wt% with respect to PP to investigate the effect of CNTs concentration on the properties of the composites.

## **2.3. Measurements and characterizations**

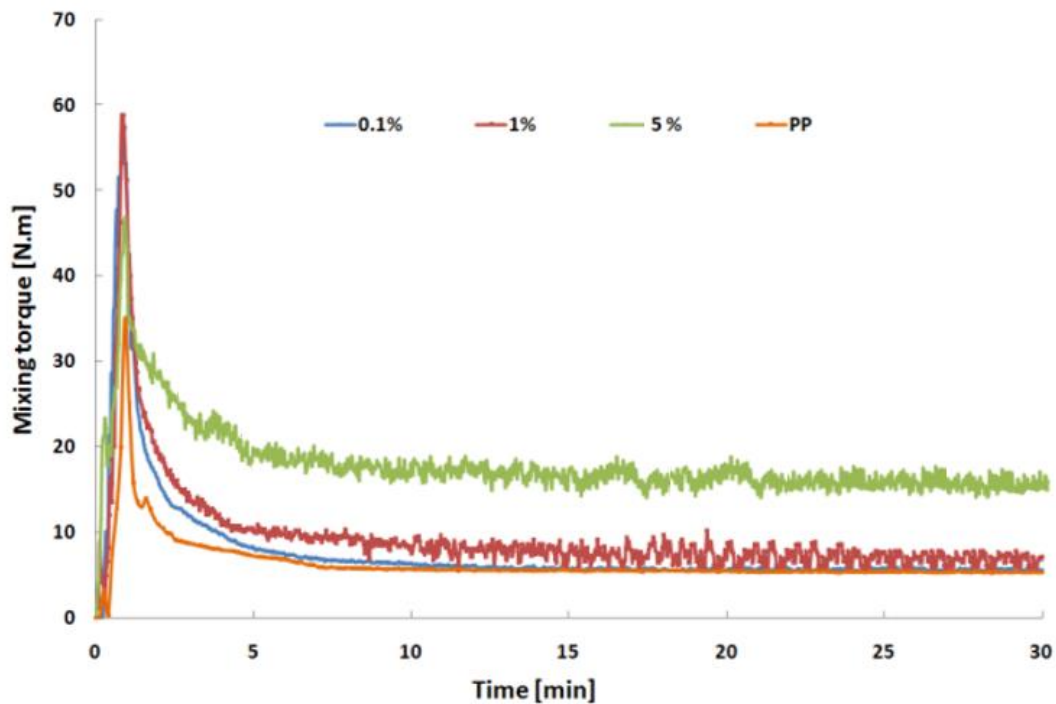
Thermo-gravimetric/differential thermal analysis (TG/DTA) of CNTs/PP composite were carried out using a thermobalance Setaram<sup>®</sup> thermal analyzer from room temperature to 500°C, at a rate of 10°C/min in a continuous argon flow. The rheological analyses were carried out using using rheometer HAAKE MARS III with a cone and plate geometry with the diameter of 35 mm and the cone angle of 2°. The shear rate has been chosen in a range from 10<sup>-1</sup> to 10<sup>2</sup>s<sup>-1</sup>. The test temperature is set from 180 to 210°C beyond the melting temperature of polypropylene and below its degradation temperature. Dynamic measurements of rheological properties were carried out using the HAAKE MARS III using parallel plate geometry (25 mm diameter and 1 mm gap). Frequencys weeps from 0.1 to 100 rad/s were performed. The morphology of CNT nanoparticles and composites were examined by scanning electron microscopy.

## **3. Results and Discussion**

### **3.1. Nano-composites elaboration**

The curves in figure 1 shows the final mixing torque variation of the PP and CNTs/PP composite (loading ratio from 0.01 to 5wt.%), vs. mixing time. Uniform mixing is achieved when the torque reaches a steady state value. However, increasing the CNTs content can increase the final mixing torque, when the CNTs content is below to 1wt.%, there is no evident difference comparing to the pure PP; when the CNTs

content is beyond 1wt.%, an evident increase of the mixing torque for the composite is observed.



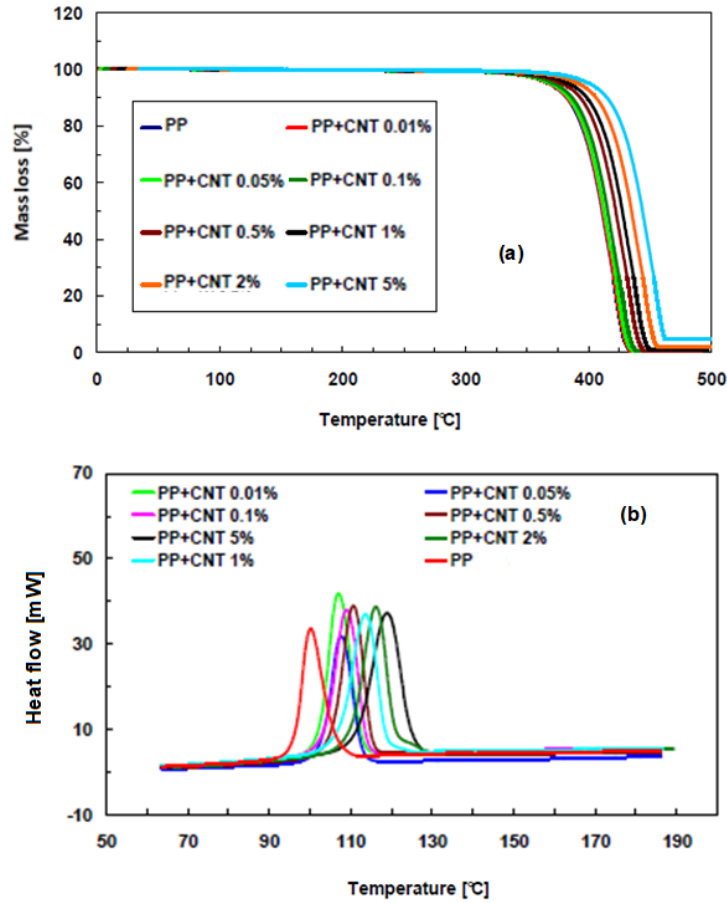
**Figure 1.** Mixing torque vs. time for PP and PP loaded CNTs at 180°C during 30 min.

### 3.2. Thermo-gravimetric analysis of nanocomposites

Thermogravimetric analysis allows assessing the behaviour of materials when subjected to the action of temperature, that's an essential tool for testing the heat resistance of polymeric materials, and therefore evaluating their thermostability. This method can also determine the actual CNTs content in the composites.

In the case of composite, an initial 98% weight loss at  $> 350^{\circ}\text{C}$  revealed the oxidation of amorphous carbon present in the sample and also attributed to the decomposition of PP and was degraded completely at  $430^{\circ}\text{C}$ . A maximum increase of  $35^{\circ}\text{C}$  was observed for the 5 wt.% composite (see Fig.2a).

The incorporation of nanoparticles CNT on PP matrix resulted in an increase in crystallization temperature ( $T_c$ ). In the case of pristine PP matrix, the  $T_c$  was observed at  $95^{\circ}\text{C}$  and was shifted to  $120^{\circ}\text{C}$  for the 5 wt.% composite. Such an effect on the  $T_c$  obtained there are also observed on the glass transition and melting temperatures. This indicates also that the thermal stability of the PP nano-particles was improved by the addition of CNT (see Fig.2ba).



**Figure 2.** Thermal properties of the CNTs/PP nanocomposite. (a) TGA and (b) DSC analysis.

### 3.3. Rheological behaviour of nano-composites

Figure 3 presents the influence of the CNTs loading ratio to the composites shear viscosity tested at 210°C. The figure shows that the viscosity of composite increases clearly with a rise of the CNTs loading ratio from 0.1wt% to 1wt%. However, for the CNTs loading ratio of 5wt%, the viscosity is too high beyond the measurement range of the rheometer. This indicates that the increasing the CNTs loading ratio results in the rise of the composites viscosity which is not conducive to the cavities filling of injection moulding process.

### 3.4. Dynamic mechanical analysis of nano-composites

Fig. 4a, it is shown that the storage modulus and loss modulus of the PP/CNTs composite increases lightly with the increase in CNTs up to 5 wt%. The results shown in Fig. 4b indicate that increasing CNTs concentration leads to a transition from convex to concave curves. Therefore, at sufficiently high concentrations the elastic modulus tends to level off as frequency goes to zero.

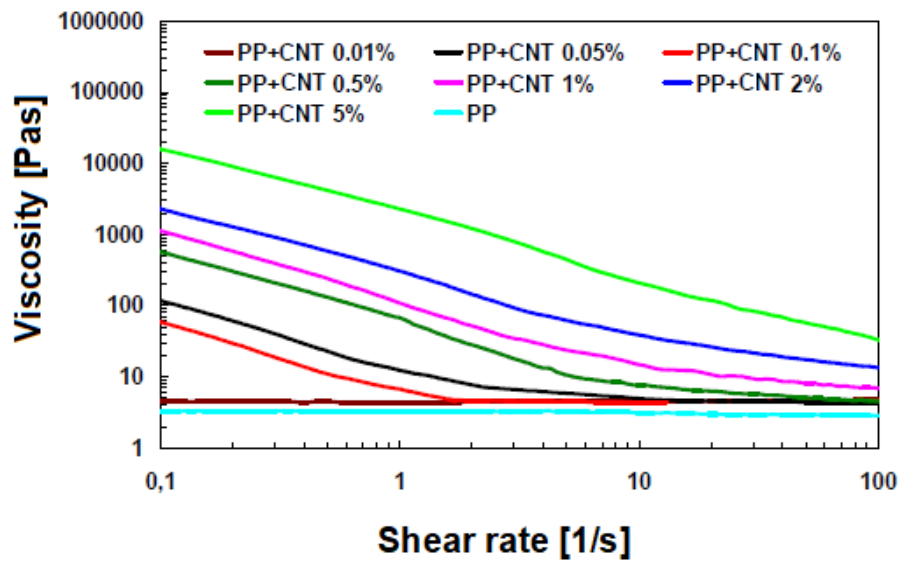


Figure 3. The shear viscosity of nanocomposite vs. shear rate obtained at 210°C.

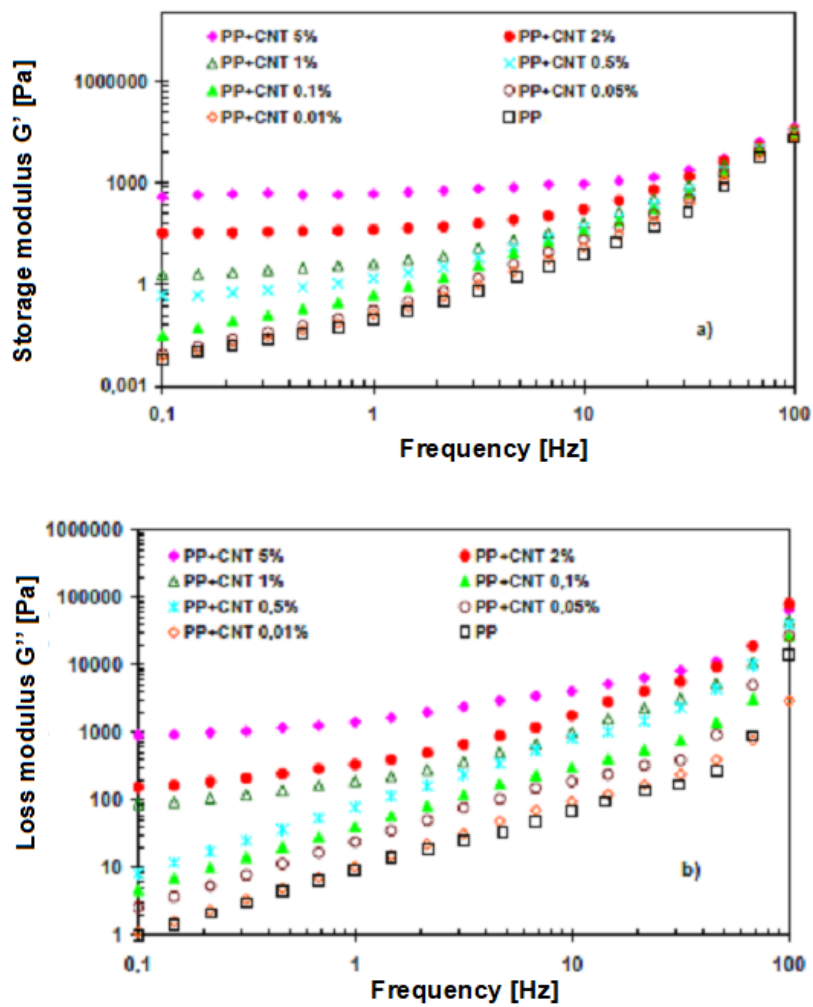
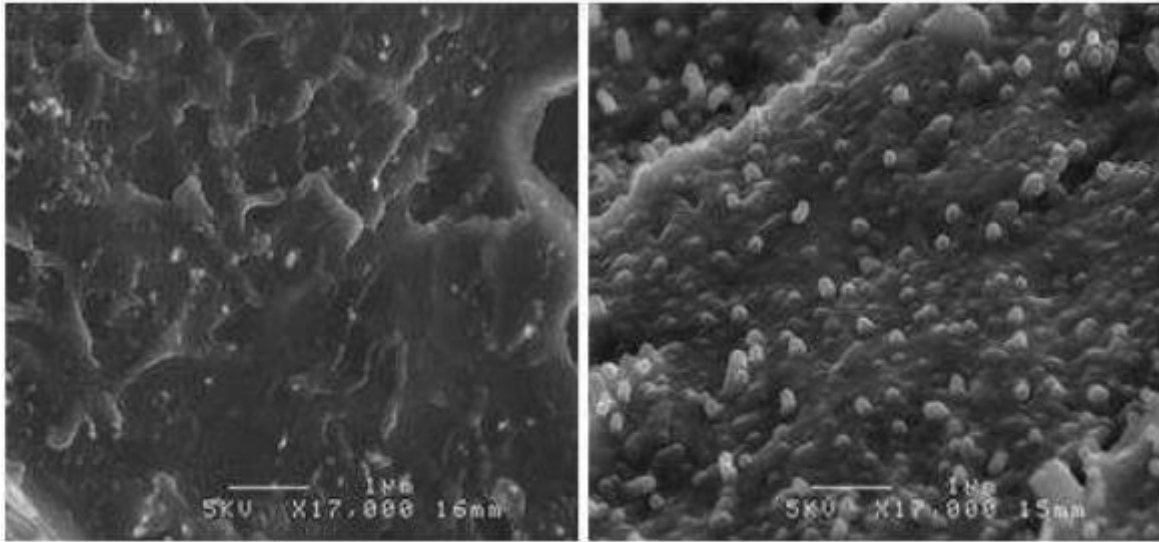


Figure 4. Variation of the visco-elastic modulus versus frequency for the nano-compositions at 180°C.



### 3.5. Morphology study

According to observations by SEM of elaborated CNT/PP nano-composites, it's difficult to observe the CNT on the surface of materials, because of the density of the matrix is so high what not allow the observation of the fillers. Only clusters of tasks are visible as small white spots (see Fig.5). The CNTs are mostly isolated from each other and uniformly distributed throughout the matrix.



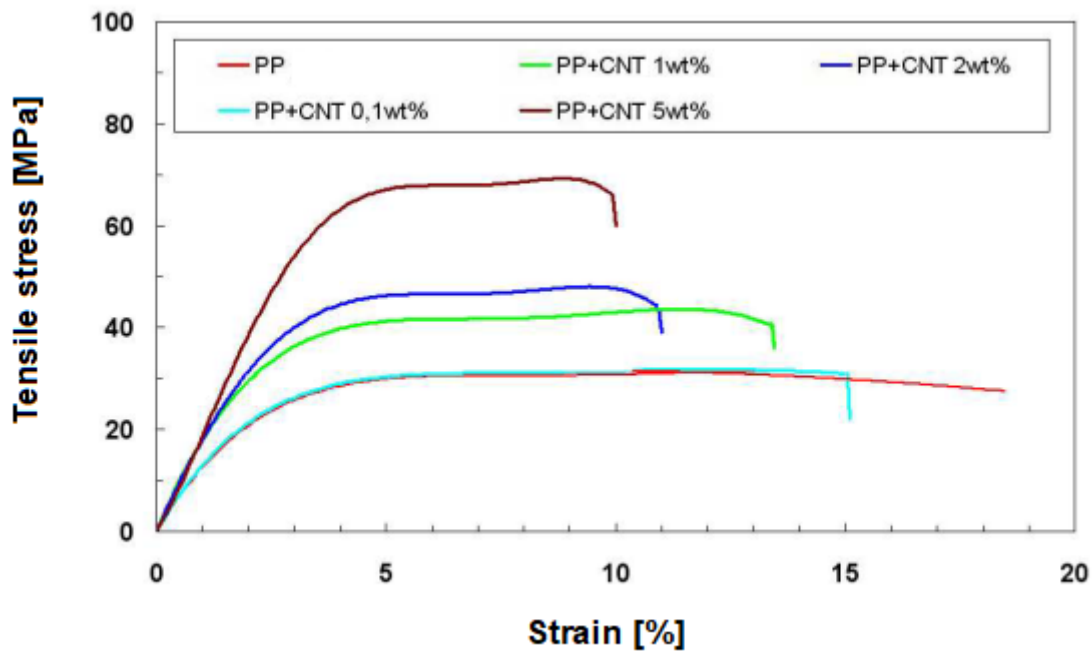
**Figure 5.** Dispersion of (a) 0.1%, (b) 2wt% CNTs in nanocomposite.

### 3.6. Mechanical characterisation of nano-composites

The effect of CNTs loading on the tensile modulus of the nanocomposites are presented in Fig. 6. Addition of 0.1% MWCNT into the composite resulted in enhancement of both modulus and strength by 11.5% and 32.8% respectively when tested at room temperature as shown in Fig. 6. This huge increment in strength might be attributed to the efficient stress transfer from the polymer matrix to the stiff CNTs through the interface. Results indicated also that this tends to stiffen and harden the nanocomposites there by reducing its resilience and toughness. The properties obtained from these stress-strain plots are then reported in Table 1.

CNT content (%)	Young Modulus [GPa]	Resistance a la traction [MPa]
0.0	1.37±0.02	31.06±0.02
0.1	1.43±0.03	31.37±0.03
1.0	1.57±0.05	43.36±0.04
2.0	1.63±0.04	47.53±0.02
5.0	1.89±0.03	68.90±0.02

**Table 1.** Properties of composites with varying CNT content at room temperatures.



**Figure 6.** Stress–strain curves for nanocomposites with various CNTs contents at room temperatures.

#### 4. Conclusion

This study is focused on the elaboration and thermo-physics characterisations of CNTs/PP nano-composite. The nano-composite specimens with 5wt% of CNTs showed improved mechanical properties, with increase in tensile strength and Young's modulus up to 11 and 33%, respectively, with respect to those of the baseline specimens. Otherwise, the experimental results showed also that the thermal stability of the nanocomposites compared with that of the baseline specimen with a fires resistance increased by more than 30°C.

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