

## EFFECT OF MULTI-WALLED CARBON NANOTUBE CONTENT ON DYNAMIC MECHANICAL PROPERTIES AND CRYSTALLINITY OF POLYPROPYLENE COMPOSITES

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This study investigates the effect of multi-walled carbon nanotube (MWCNT) content on the dynamic mechanical properties and crystallinity of polypropylene (PP). Carbon nanotubes are promising additives for polymer composites due to their excellent mechanical, electrical, and thermal properties. Polypropylene/multi-walled carbon nanotube (PP/MWCNT) composites were produced in single and double screw extruders. The composites contained 0.5, 2, 3 and 5 wt% multi walled carbon nanotubes. The effect of MWCNT addition on the thermal transitions of the PP was investigated by differential scanning calorimetry (DSC) measurements. Dynamic mechanical analysis (DMA) studies revealed an enhancement of the storage modulus.

**Keywords:** carbon nanotubes, polypropylene, composites, dynamic mechanical analysis, crystallization

### Introduction

The reinforcement of polymers with nano-scaled fillers developed a new class of advanced multifunctional materials with improved properties, used in many fields ranging from microelectronics to aerospace engineering [1,2]. Among nanofillers, carbon nanotubes (CNTs) are an especially attractive class of additives because of their exceptional mechanical, thermal and electrical properties. Polyolefins are, on the other hand, among the most versatile polymer matrices such as polypropylene, because of their good balance between properties and cost, low density and ease in processability [3]. Polypropylene (PP) is one of the most commonly used thermoplastic polymers which has been utilized in automobiles, appliances, construction, household goods, etc.

Carbon nanotubes were discovered in the soot of arch discharge by Sumio Iijima in 1991 [4]. Carbon nanotubes are allotropes of carbon and members of the fullerene structural family. CNTs are promising additives for polymer composites due to their excellent mechanical, electrical and thermal properties. The special mechanical properties are due to the strong bonding between the carbon atoms that form the carbene plane. The tensile strength of carbon nanotubes is high, 75-times higher than of steel filaments of the same size, and even 15-times higher than of carbon fibers. On the other hand, the density of carbon nanotubes is one sixth of steel. Their densities can be as low as 1.3 g/cm<sup>3</sup>. These facts give excellent opportunities to produce very strong materials which are light at the same time.

Several processing methods are available for the production of polymer/CNT composites, such as melt mixing, solution casting and *in situ* polymerization [6]. Among them, melt mixing is particularly desirable as it combines speed with simplicity. Furthermore, it is free of solvents and contaminants and the required equipment is already available in the plastic industry. In all the techniques mentioned above, a homogeneous dispersion and good interfacial adhesion are crucial for the successful preparation of nanocomposites [7,8].

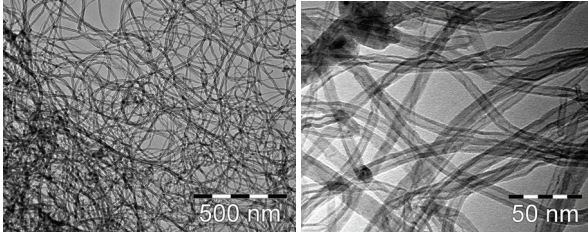
Extrusion is the most effective and most important technology in polymer processing. This makes the thermoplastic polymer plastic, homogenizes its viscous melt, and degasifies it, if necessary. After this, the polymer is compressed, extruded in an open instrument of constant diameter and cooled down. Thus, polymer products of constant diameter can be produced in the desired length, in continuous run. [6]

In this work, the dynamic mechanical properties and the thermal transitions of polypropylene blended with various contents of MWCNT were investigated. Similar research was carried out by Logakis et al. [9] and Teng et al. [10].

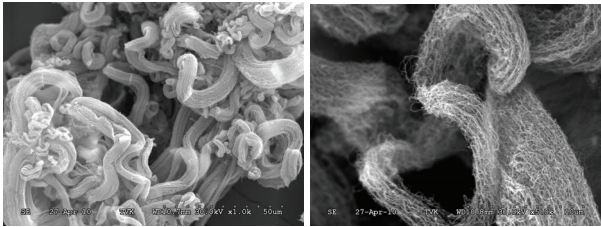
### Experimental

Multi-walled carbon nanotubes (MWCNT) were produced at 700 °C by chemical vapor deposition (CVD) process over Fe-Co bimetallic catalyst at the Institutional Department of Chemical Engineering (Institute of Chemical and Process Engineering, University of

Pannonia). The purity of MWCNT was ~90 wt%. According to transmission electron microscope (TEM) images, the diameter of the tubes is between 10 and 20 nm (*Fig. 1*). The length of the tubes cannot be precisely measured. According to the scanning electron microscope (SEM) images, the length of the tubes is greater than 50  $\mu\text{m}$  (*Fig. 2*). Polypropylene (PP) homopolymer (H116F, melt flow rate 28.0 g/10 min at 190 °C, 2.16 kg) was used as polymer matrix.



*Figure 1:* TEM images of multi-walled carbon nanotubes



*Figure 2:* SEM images of multi-walled carbon nanotubes

Polypropylene-based composites were prepared with a Brabender-type single screw extruder (SSE, zone temperatures: 1: 195 °C, 2: 200 °C, 3: 205 °C, 4: 210 °C, revolutions per minute: 40), and with a Werner & Pfleiderer-type double screw extruder (DSE, zone temperatures: 1: 195 °C, 2: 205 °C, 3: 210 °C, 4: 210 °C, 5: 210 °C, 6: 210 °C revolutions per minute: 100), to decide which method gives better results. The composites contained MWCNT in different quantities (0.5, 2, 3 and 5 wt%). The content of the composites is summarized in *Table 1*.

*Table 1:* The content of the composites

Sample	PP (wt%)	MWCNT (wt%)
PP	100	
SSE/0.5	99.5	0.5
SSE/2	98	2
SSE/3	97	3
SSE/5	95	5
DSE/0.5	99.5	0.5
DSE/2	98	2
DSE/3	97	3
DSE/5	95	5

Specimens for dynamic mechanical analysis (DMA) testing were compression molded under a pressure of 15 MPa for 5 min, at 170 °C. Slabs were prepared with a thickness of 2 mm.

Differential scanning calorimetry (DSC) measurements were carried out in the temperature range of 30 to 200 °C.

The sample was heated in two stages in nitrogen environment. In the first run, the sample was heated from 30 to 200 °C at a heating rate of 10 °C/min and held at 200 °C for 1 minute. Then the sample was cooled to 30 °C at a cooling rate of 10 °C/min to release the internal stress of the sample. In the second run, the first run procedure was repeated.

Dynamic mechanical analysis (DMA) was performed in the two-point bend mode. The thickness of the specimens was 2 mm. The temperature scan ranged from -155 to 100 °C, at a heating rate of 2 °C/min, the frequency was 1 Hz, under a constant nitrogen gas flow rate of 20 cm<sup>3</sup>/min.

## Results

The effect of MWCNT addition on the thermal transitions of the PP was investigated by differential scanning calorimetry (DSC) measurements.

*Table 2* summarizes the peak melting point, the final melting points and the heats of melting of the composites.

*Table 2:* Peak melting points, final melting points and heats of melting of the composites

Sample	peak melting point (°C)	final melting point (°C)	heat of melting (J/g)
PP	163.9	170.9	120.2
SSE/0.5	165.7	170.7	130.1
SSE/2	165.7	169.9	127.1
SSE/3	166.1	171.0	126.8
SSE/5	165.3	169.4	115.0
DSE/0.5	165.8	170.4	124.7
DSE/2	167.0	172.4	127.1
DSE/3	168.0	172.5	129.7
DSE/5	168.4	174.3	129.9

As it can be seen clearly, the composites do not differ significantly in their melting properties when using a single screw extruder. When using a twin screw extruder to prepare the composites, the peak and final melting points were rising with the rising carbon nanotube content. The same are true of the heats of melting of the composites. *Table 3* gives the initial and peak temperatures of crystallization of the composites. As it can also be seen, there is no significant change in the crystallization properties of the composites in the case of the single screw extruder. When using a twin screw extruder to prepare the composites, the initial and peak crystallization temperatures were rising with the rising carbon nanotube content. The extent of rise is illustrated in *Fig. 3*.

The rise in melting and crystallization temperatures of the composites is due to the nucleating effect of the MWCNTs. The effect is realized in the case of the single screw extruder, but not consequently because there is no relationship with the MWCNT concentration. This is probably due to the low homogeneity of the carbon nanotubes in the matrix. For composites prepared with the twin screw extruder, on the other hand, the nucleating effect is increasing with the increasing carbon nanotube

content which can be attributed to the more homogenic dispersion of the tubes in the matrix.

Table 3: Initial and peak temperatures of crystallization of the composites

Sample	initial temperature of crystallization (°C)	peak temperature of crystallization (°C)
PP	122.6	116.5
SSE/0.5	128.4	123.7
SSE/2	137.7	124.0
SSE/3	132.0	124.3
SSE/5	136.0	124.9
DSE/0.5	129.6	125.7
DSE/2	133.2	128.6
DSE/3	135.9	131.0
DSE/5	138.1	132.2

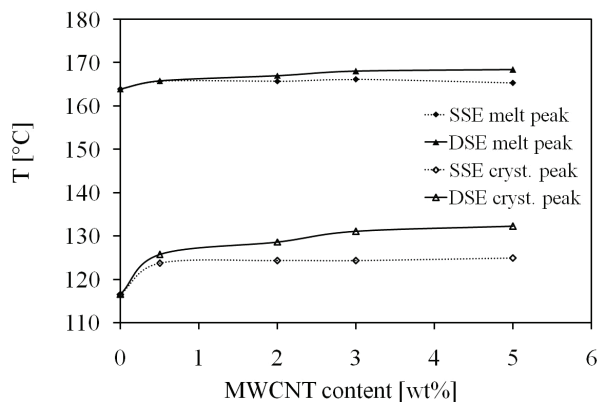


Figure 3: Peak melting and peak crystallization temperatures of the composites

Dynamic storage modulus ( $E'$ ) and tangent delta ( $\tan \delta$ ) of the composites were analyzed with dynamic mechanical analysis (DMA).  $E'$  of the composites increases in the glassy state and the rubbery state on addition of carbon nanotubes (Table 4).

The increase of the value of the storage modulus in the glassy phase ( $E'$ ) is small in the case of the composites produced with the single screw extruder. The value of the storage modulus in the glassy phase increases significantly with the increasing carbon nanotubes content in the case of the composites produced with the single screw extruder. The increase is 45% at 2wt% CNT, and 75% at 5wt% CNT. Similar results were obtained for the value of  $E'$  in the elastic phase. The value of  $E'$  did almost not change when using the single screw extruder, while it increased when using the twin screw extruder. The increase is 110% at 3wt% nanotubes content.

Table 4 shows the glass temperature ( $T_g$ ) of the composites. The peaks which appear in the tangent delta ( $\tan \delta$ ) correspond to  $T_g$  values. The glass transition temperatures of the composites produced with the single screw extruder did not change significantly. A clear-cut tendency with changing the carbon nanotubes content cannot be determined. The temperature of glass transition of the composites produced with the twin screw extruder decreased.

Table 4: Dynamic storage modulus ( $E'$ ) in the glassy and in the rubbery state for the pure PP matrix and PP/MWCNT composites.

Sample	$E'$ in the glassy state (at $-40^\circ\text{C}$ ) (GPa)	$E'$ in the rubbery state (at $60^\circ\text{C}$ ) (GPa)	$T_g$ ( $^\circ\text{C}$ )
PP	3.1	0.9	5.9
SSE/0.5	3.4	1.0	5.5
SSE/2	3.5	1.1	6.2
SSE/3	3.7	1.2	5.1
SSE/5	3.8	1.2	5.4
DSE/0.5	3.6	1.2	5.0
DSE/2	4.5	1.3	4.1
DSE/3	5.1	1.9	3.0
DSE/5	5.4	2.2	2.4

## Conclusions

Polypropylene/multi walled carbon nanotube composites were produced in single and double screw extruders. The composites contained 0.5, 2, 3 and 5 wt% multi-walled carbon nanotube. The melting points, the temperatures of crystallization and the heats of melting of the composites were investigated by differential scanning calorimetry (DSC) measurements. The composites do not differ significantly in their melting and crystallization properties when using a single screw extruder. When using a twin screw extruder to prepare the composites, the melting points and the temperature of crystallization were rising with the rising carbon nanotube content. The same are true of the heats of melting of the composites.

The dynamic storage modulus and the glass temperature of the composites were investigated with dynamic mechanical analysis (DMA). The  $E'$  and  $T_g$  values of the composites produced with the single screw extruder changed almost unnoticeably. The  $E'$  value of the composites produced with the twin screw extruder rose significantly with the rising carbon nanotubes content while the temperature of glass transition decreased.

## ACKNOWLEDGMENT

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