SWCNT TUBALL^{TM} as a universal conductive additive in plastics

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ABSTRACT

In this report, the development of electro-conductive polyethylene filled with SWCNT TUBALL^{TM} is demonstrated. The observed percolation threshold of TUBALL^{TM} (0.01-0.1 wt.%) appears to be very small in comparison with other commercially available conductive fillers. Moreover, the plastics filled with TUBALL^{TM} demonstrate the improved physico-mechanical properties. The electrical conductivity and improved physico-mechanical characteristics of plastics obtained with low loading of TUBALL^{TM} SWCNTs make this additive very promising in plastic industry.

Keywords: single-walled carbon nanotubes, CNT, conductive polymers

1 INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [1], this material attracts a great interest due to its unique electrical [2] and physico-mechanical properties [3]. Single-walled carbon nanotubes (SWCNTs) are the most promising conductive agent for plastics due to their lower percolation threshold compared to carbon black, carbon nanofibers and multi-walled carbon nanotubes. However, the industrial applications of SWCNTs have not been considered yet due to their extremely high cost. The appearance of the TUBALL^{TM}, which is SWCNTs produced by OCSiAl (www.ocsial.com), made use this material cost-effective.

2 TUBALL^{TM} SWCNT PROPERTIES

TUBALL^{TM} is high quality SWCNTs. The quantitative information concerning physico-chemical characteristics and purity of TUBALL^{TM} material are summarized in Table 1. A number of physical methods applied in our study shows high content and quality of the SWCNTs in TUBALL^{TM}, with concentration of other impurities being extremely low.

Table 1. The main parameters of TUBALL^{TM}

Specification	**Unit**	**Value**	**Evaluation metod**
Carbon purity	Wt.%	> 85	TGA, EDX
CNT	Wt.%	≥ 75	TEM, TGA
Number of layers	Unit	1	TEM
Mean diameter	nm	1.5±0.4	Raman, TEM
Length	μm	>5	AFM
Metal impurities	Wt.%	<15	EDX, TGA

As it's seen from the high-resolution TEM image of TUBALL^{TM} powder (Figure 1), this material consists of thin bundles of SWCNTs with a diameter of less than 50 nm. Low content of amorphous carbon and metal particles observed by HRTEM also confirms high quality of TUBALL^{TM} SWCNTs.

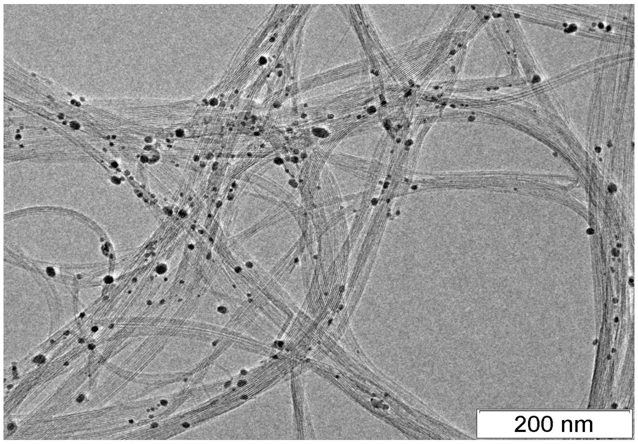

Figure 1. High resolution TEM image of SWCNT

High quality of TUBALL^{TM} SWCNTs can be confirmed by high value of G/D intensity ratio in Raman spectrum (Figure 2).

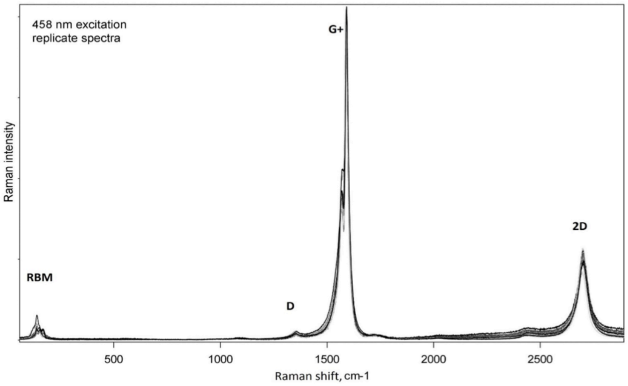

Figure 2. Raman spectrum of SWCNT.

3 EXPERIMENTAL

As mentioned before, SWCNTs have extrimely low percolation threshold in comparison with other conductive fillers such as carbon black, carbon nanofibers and multi-walled carbon nanotubes. In this report, we demonstrate several approaches for SWCNTs loading into polyethylene (PE) based on extrusion of PE with SWCNTs. In this work, co-rotating twin screw extruder with L/D=40 was used. PE was used as recived - LLDPE Sabic with MFI=20 g/10min at 190 °C and 2.16 kg. SWCNTs were provided by OCSiAl company.

It is well known that SWCNTs have a strong tendency to agglomeration making challenge to achieve a percolation threshold at low SWCNTs concentration values. In order to avoid this issue, we studied several extrusion based approaches of SWCNTs loading into PE matrix. These approaches could be divided into two main directions. The first approach is direct compounding, i.e. direct melt mixing of SWCNTs with PE achieving a percolation threshold at 0.1 wt.%. The second approach includes the preparation of concentrate, which contains 1-2 wt.% of SWCNTs in PE, with further dilution of this concentrate with pure PE through extrusion reaching a percolation threshold also at 0.1 wt.% of SWCNTs.

Direct melt mixing of PE is realized as extrusion PE granules with as-recieved SWCNTs powder. On the other hand, direct melt mixing is prepared for PE powder coated by SWCNTs through the water dispersion. For this, SWCNTs water dispersion is introduced to PE powder with further water evaporation at 70 °C. Table 2 shows resistivity of PE samples filled with 0.1 wt.% of SWCNTs using different approaches. It is shown that the loading of PE with SWCNTs using masterbatching and coating with water based dispersion prepared without using surfactant. However, a sample obtained using the coating through the water dispersion of SWCNTs, prepared using surfactant, demonstrates fully dielectric behavior. This fact shows that surfactant can cover SWCNTs surface avoiding contacts between them.

Table 2. Resistivity of PE loaded with 0.1 wt.% of SWCNTs, extrusion at 200 °C and 300 rpm.

Approach	**Melt mixing**		**Coating**	
	Granules	Masterbatch	-	PVP
R, Ω*cm	10^6	10^4	10^4	10^{12}

Electrical resistivity of PE filled with 0.1 wt.% of SWCNTs using direct melt mixing of PE granules with SWCNTs powder, a coating of PE powder with SWCNTs water dispersion and masterbatching as a function of extruder screw speed is shown on Fig. 3. As it can be seen on the curves, the samples prepared through the coating and masterbatching demonstrate low resistivity at all screw speeds, while the sample prepared using PE granules has higher resistivity at lower screw speed conditions. Such behavior can be explaned by the difficulties of mixing of PE granules with SWCNTs powder in comparison with PE powder due to lower size of PE powder particle.

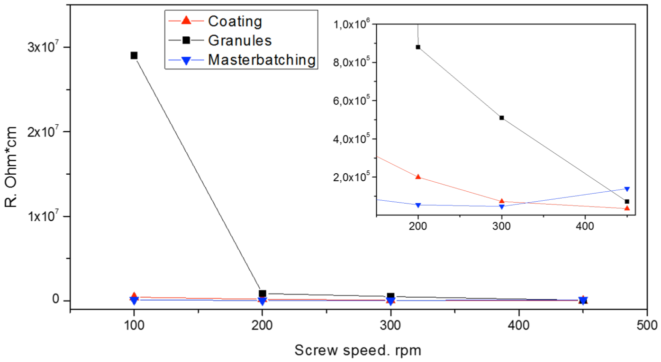

Figure 3. Resistance of polyethylene filled with 0.1 wt.% of SWCNTs obtained using different approached as a function of extrusion screw speed.

Physico-mechanical characteristics of PE filled with 0.1 wt.% of SWCNTs using masterbatching are presented on Fig. 4. SWCNTs allow increasing, for example, an elastic modulus up to 28 %. However, the loading of SWCNTs results in decrease of alongation at break. This behavior is typical for all realogical additives.

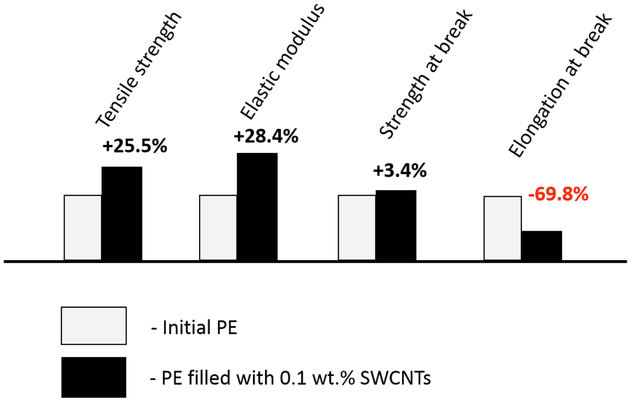

Figure 4. Scheme of physico-mechanical characteristics of PE filled with 0.1 wt.% of SWCNTs using masterbatchng approach in comparison with pure PE.

4 CONCLUSIONS

In this paper, we demonstrate application of SWCNTs TUBALL$^{\text{TM}}$ in polyethylene. SWCNTs TUBALL$^{\text{TM}}$ allows achieving conductive polyetylene with improved physico-mechanical properties. This carbon nanomaterial recently appeared on the marked could be introduced into PE with a number of approaches such as various direct melt mixing procedures and through the masterbatchnig, which icould be a critical point in terms of industrial applications.

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