Carbon Nanotubes as a New Class of Flame Retardants for Polymers

Dr. Günter Beyer
Kabelwerk EUPEN AG
B - 4700 Eupen, Belgium
+ 32 87 59 7000 · guenter_beyer@eupen.com

Abstract

Carbon nanotubes (MWCNTs or SWCNTs) were used as nanofillers in polyethylene. Only MWCNTs reduced the heat release rates caused by polymer degradation. MWCNTs can be more effective in heat release reduction than organoclays. The char generated by the nanofiller blend "MWCNTs and organoclays" as a synergistic flame retardant system in EVA was improved compared to the char generated by organoclay based nanocomposites. Initial results indicated that there was a strengthening effect of the char by MWNTs. The synergistic improvement for heat release reduction by a blend of the two nanofillers "MWCNTs and organoclays" was used for the development of a flame retardant cable compound. 1.5 kg of MWCNTs were compounded on a BUSS ko-kneader to generate 60 kg of a nanocomposite based on the nanofiller blend. The flame retardant properties of insulated wires made either by the nanofiller blend or by "classical" organoclays were measured.

Keywords

Carbon nanotubes, MWCNT, SWCNT, nanocomposites, organoclays, cone calorimeter, flame retardancy, cables, wires, fire science

1. Introduction

Nanocomposites show tremendous property enhancements compared to pure polymers. The content of the well-known organoclays (modified layered silicates) is often added at a level between 2 weight-% and 10 weight-%.

A highly interesting property exhibited by polymer-layered silicate nanocomposites concerns their ability to promote flame retardancy at very low filling levels. The formation of a thermal insulating and low permeable char to volatile combustion products caused by a fire is responsible for these improved properties [1-3]. The low filler content in nanocomposites for the improvements in flame retardancy are highly attractive for the industry because end-products can be made cheaper and easier to process.

Beside the "classical" organoclays, we reported for the first time at the last BCC conference in 2002 about carbon nanotubes as a new class of nanostructured flame retardants for EVA [4]. Also NIST published very similar results for PP [5].

2. Materials and Process

In our experiments, we used a commercially available montmorillonite modified by quaternary dimethyl-dioctadecylammonium cations (organoclay). Pure and crude multi wall carbon nanotubes (MWCNTs) and single wall carbon nanotubes (SWCNTs) were produced by NANOCYL / Belgium, a company established by the research group of Prof. Janos B. Nagy from the University of Namur / Belgium. LDPE from BP was used as a non-polar polymer matrix for MWCNTs and SWCNTs. Aluminium trihydrate (ATH) Martinal OL 104 LE by ALBEMARLE was used as a conventional flame retardant. Mixing was done on several compounding machines. A Brabender mixer as a discontinuous compounding machine was used at 45 rpm to generate filled PE with MWCNTs and SWCNTs. A laboratory rolling mill was used to compound different MWCNT / organoclay based cable formulations to optimize their fire properties. Also a BUSS ko-kneader (with a rotating and simultaneously oscillating screw, 11 L/D, 46 mm screw diameter) at POLYONE's plant in Melle/Germany was used as a continuous compounding machine to produce 60 kg of an optimized MWCNT/organoclay compound. Processing temperature was 160°C for the BUSS-extruder and the rolling mill. The Brabender mixing temperature was 180°C for LDPE. A 80 mm 20 L/D single screw cable extruder was used to produce an insulated flexible 2.5 mm^2 copper wire with 0.86 mm wall-thickness for the flame retardant insulation. The cone calorimeter experiments were done at 35 kW/m^2 heat flux with horizontal orientation of the samples.

3. Properties and applications of carbon nanotubes

Carbon nanotubes (NTs) are tubular derivatives of fullerenes. They were first observed in arc discharge methods and exhibit properties which are quite different from those of the closed cage fullerenes such as C60, C70, C76 etc. The special topologies are responsible for the unique and interesting properties of carbon nanotubes. As novel carbon materials, the carbon nanotubes are of great interest within the field of material science research. Due to their high mechanical strength, capillary properties and remarkable electronic structures, a wide range of potential uses has been reported. Typical applications for the NTs are supports for metals in the field of heterogeneous catalysis, material for hydrogen storage, composite materials in polymer science, and for immobilization of proteins and enzymes. Several techniques like arc discharge, laser ablation, catalytic methods and others are developed for the production of NTs. Many material science researchers are working on development of methods for the production of NTs in large-scale to realize their potential applications. NTs can consist of one (single wall carbon nanotubes, SWCNTs) or more (multi wall carbon nanotubes, MWCNTs) cylindrical shells of graphitic sheets. Each carbon is completely bonded to three neighboring carbon atoms through sp^2 hybridization to form a seamless shell. It is reported [6] that polymer degradation can be retarded by carbon nanotubes as indicated by thermogravimetric analysis. In PVOH, a loading level of 20 weight-% MWCNTs shifts the beginning of the polymer degradation and also the single degradation peak to higher temperatures.

4. Synthesis of carbon nanotubes and compounds

Crude MWCNTs and SWCNTs were produced by catalytic decomposition of acetylene and contained the used catalysts and other by-products from the nanotube synthesis. The by-products are amorphous carbon, pyrolytic carbon, carbon nanoparticles, fullerenes, metal nanoparticles encapsulated in carbon, carbon fibres etc. The spent catalysts are oxides, mixed oxides, aluminosilicates, zeolites, oxycarbides, mixed oxycarbides, carbonates, metal hydroxides, metal nanoparticles etc. Crude and purified nanotubes samples were used to prepare the nanocomposites. Crude SWCNTs contained Co and MgO. Purified SWCNTs were synthesized from crude SWCNTs by dissolution of the catalyst support in concentrated HCl, purification by air oxidation at 300°C and then drying at 120 °C in an air oven. Crude MWCNTs contained Co, Fe and alumina. Purified MWCNTs were synthesized from crude MWCNTs by dissolution of the catalyst support in concentrated NaOH, dissolution of the metal catalyst in concentrated HCl, drying at 120 °C in an air oven and additionally drying at 500 °C under vacuum.

Compounds of SWCNTs and MWCNTs in LDPE BPD 8063 were melt blended in a Brabender mixing chamber according to the formulations indicated in Table 1 and Table 2. The samples were pressed to plates of 100x100x3mm and the reductions of heat release were measured by cone calorimeter, Figure 1 and Figure 2.

The results from the cone measurements of different carbon nanotubes in LDPE are :

- SWCNTs do not act as flame retardants in LDPE
- MWCNTs act as flame retardants in LDPE with no reduction in "time to ignition" (in contrast to organoclays) and with reduction of heat release
- Crude MWCNTs have similar heat release reduction as purified MWCNTs

Table 1 : SWCNT compounds in LDPE

Sample description	LDPE (weight-%)	SWCNT (weight-%)	
		Purified	Crude
BPD 8063	100.0	-	-
5 SWCNT	95.0	5	-
10 SWCNT	90.0	10	-
5 crude SWCNT	95.0	-	5
10 crude SWCNT	90.0	-	10

Table 2 : MWCNT compounds in LDPE

Sample description	LDPE (weight-%)	MWCNT (weight-%)	
		Purified	Crude
BPD 8063	100.0	-	-
5 MWCNT	95.0	5	-
10 MWCNT	90.0	10	-
5 crude MWCNT	95.0	-	5
10 crude MWCNT	90.0	-	10

Figure 1 : SWCNTs in LDPE

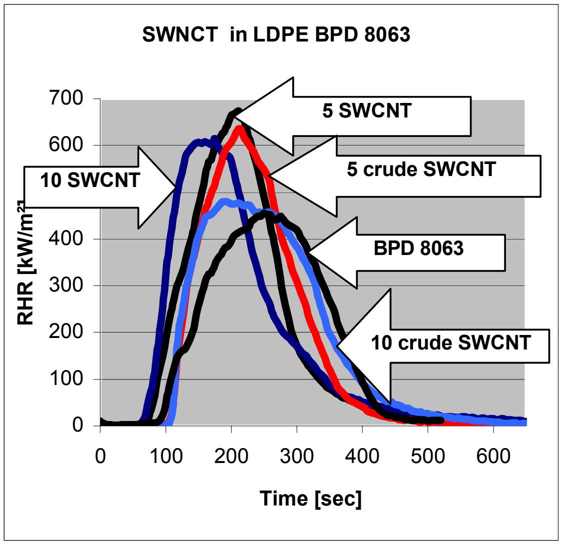
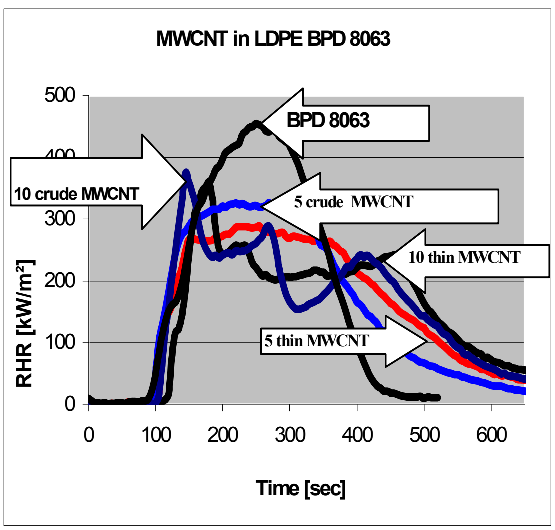


Figure 2 :   MWCNTs in LDPE



5. MWCNTs / organoclay flame based retardancy

In 2002 we reported for the first time worldwide that MWCNTs in EVA reduced the heat release of the virgin polymer. An additional synergistic improvement of the heat release by blending both nanofillers MWCNTs and organoclays resulted in a perfectly closed char without any cracks. In contrast, the same formulations with only organoclays generated a char with many cracks and therefore higher heat release values [4]. Our results with the new nanofiller combination indicated that, within the burnt samples, the char was strengthened by the very long L/D ratio of the MWCNTs thus preventing the char from cracking [Figure 3 and Figure 4].

Figure 3 :   EVA nanocomposite with 5 phr organoclays

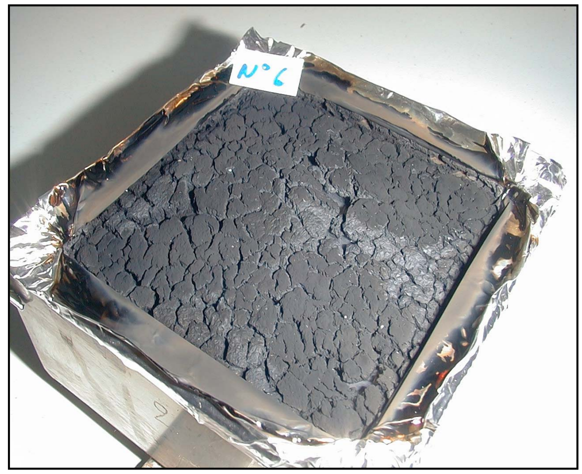
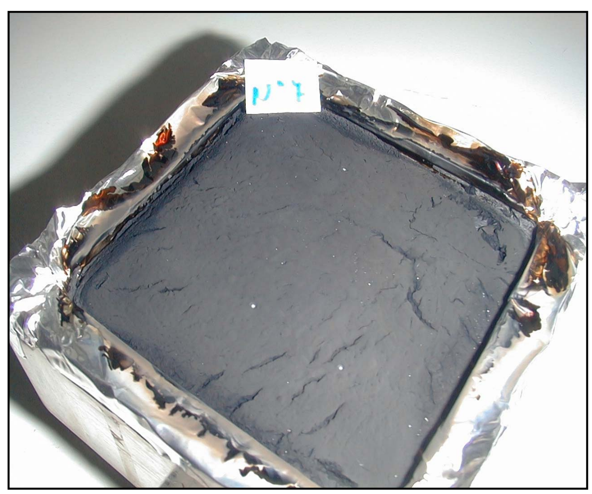


Figure 4 :   EVA nanocomposites with 2,5 phr organoclays and 2,5 phr MWCNTs



6. From theory to reality - a cable with the new FR-system “MWCNTs / organoclays”

We were interested within our research activities to transform the results for the synergistic nanofiller-based FR-system “MWCNTs / organoclays” to real products. Therefore, we received from the carbon nanotube supplier NANOCYL 1.5 kg of MWCNTs. To produce a flame retardant insulated wire by a real cable production extruder we needed a minimum of approximately 60 kg of compound to fill up the extruder and to run a small insulated wire production.

In a first experiment, we checked whether we can transform without problems the nanofiller blend system “MWCNTs / organoclays” from the tested polymer EVA to a real cable compound. We used a well running only organoclay based cable compound named compound 1 and changed stepwise the weight ratio between the two nanofillers. The sum of both nanofillers always remained constant [Table 3] within the cable compounds. Compounding was done on a rolling mill and the reductions of heat release rates for the 3 compounds were measured. The results clearly indicated that, for the nanofiller blend, the first peak of heat release was maximally reduced. Also the second peak heat release was observed at longest time for the formulation with the nanofiller blend, indicating that the char was less cracked (more stable in time). Thus, we used a 1:1 blend of MWCNTs and organoclays (compound 2 A, see Table 3) for the cable compound formulation. This allowed us to produce the required quantity of the flame retardant cable compound.

Compounding of the formulation 2 A was done on a 46 mm 11 L/D BUSS ko-kneader and 60 kg was produced without any processing problems. Processing on the BUSS ko-kneader also improved the heat release rates compared to the corresponding rolling mill compounding, maybe by better filler dispersion.

2 insulated wires with identical geometric parameters were produced on a 80 mm 20 L/D single cable extruder. For one wire the insulation was compound 1 (filler combination by ATH / organoclay) and for the other wire the optimized insulation compound 2 A (filler combination by ATH / organoclay / MWCNTs) was used as insulation.

The MWCNT-based compound 2 A showed a remarkable increased viscosity compared to the standard nanocomposite compound 1 indicated by reduced rpm of the screw and increased power take-up by the extruder motor; high pressure capillary viscosimeter also showed a higher viscosity for the compound 2 A for all shear rates up to 3000 s^{-1}.

A small scale fire test according to IEC 60332-1 (Bunsen burner flames attacked the insulation) was very similar to both insulated wires. No dripping of burning polymer was noted and the charred lengths were identical. But the char of the insulation made with the compound 2 A was much less cracked compared to the char generated from the compound 1.

We measured furthermore the heat release rates and “times to ignition” of the 2 insulated wires by cone calorimeter. The wires were cutted in samples of 10 cm and the standard cone sample holder was filled up with the cables pieces. We mounted the wires by building up 1 layer of wires with no gap between them [7] and the ends of the wires were not sealed; we called this mounting a single layer design. We also put together 4 cutted wires with no sealing of the ends simulating an unjacketed cable. An aramid fibre binder was used to maintain the integrity of the bundles; this mounting was called a bundle design [Figure 5 and Figure 6].

Table 3 : Blends of MWCNT / organoclay compounds in cable compound formulations

	Composition
Compound 1	Technical cable compound (EVA / PE / ATH / organoclay / processing additives)
Compound 2 A	Same formulation as compound 1, but substitution of 50 % organoclay by the same amount of MWCNTs
Compound 2 B	Same formulation as compound 1, but substitution of 100 % organoclay by the same amount of MWCNTs

Figure 5: Insulated wire mounting design (single layer design) for cone tests

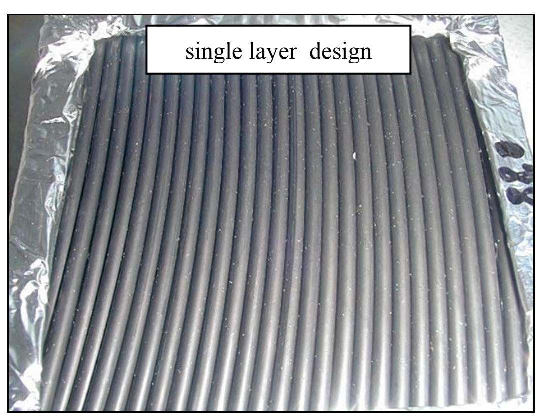


Figure 6: Insulated wire mounting design (bundle design) for cone tests

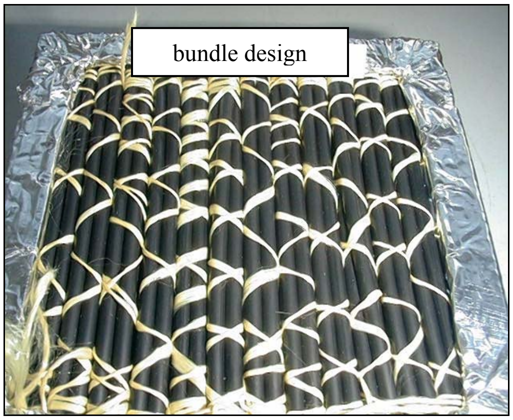
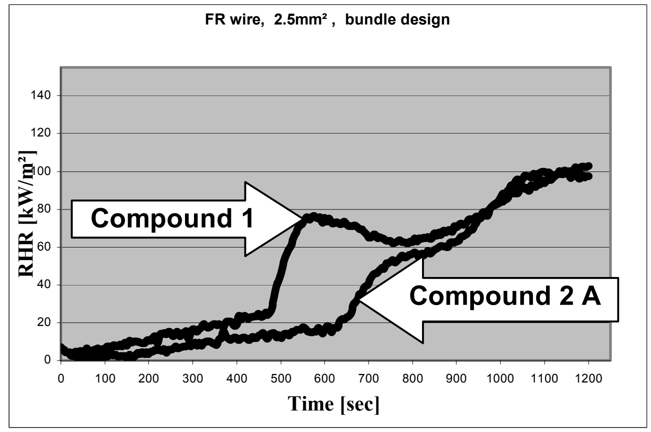
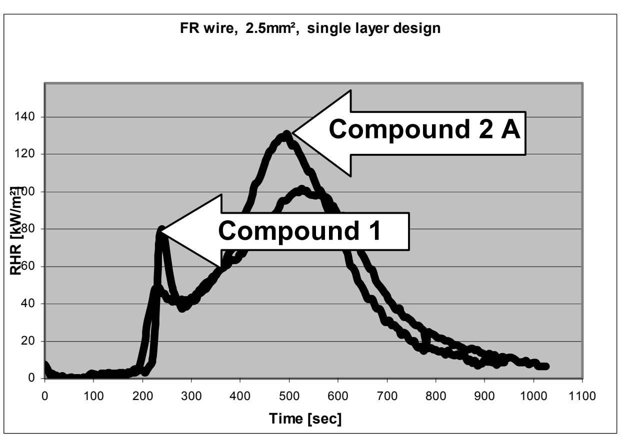


Figure 8: Cone datas for bundled insulated wire mounting design



Both designs demonstrated quite different cone calorimeter results (Figure 7 and 8). For the single layer design the duration for the tests was ok and within 1200 seconds the tests were finished. The design is also known for some end product applications. A first remarkable peak at 213 seconds was only observed for compound 1. For the bundle design the duration for the cone tests was very long due to the insulation effect of the first charred layers to the underneath located wires; therefore we stopped the trials after 1200 seconds. This mounting design is also representative for many end product applications. In contrast to compound 1, the heat release as the most important single factor in a fire (driving force of the fire) has the lowest values for the nanofiller blend within 600 sec.

Figure 7: Cone datas for single layer insulated wire mounting design



7. Conclusion

Nanofillers based on multi wall carbon nanotubes act as very efficient flame retardants at low filler contents in the non-polar polymer polyethylene. In contrast single wall carbon nanotubes do not show any improvements on flame retardancy.

An optimized formulation for insulated wire applications was developed based on the nanofiller blend “multi wall carbon nanotubes / organoclays” and 60 kgr compound were made on a BUSS ko-kneader.

With an optimized cable compound an insulated wire was produced on a 80 mm 20 L/D single screw cable extruder. Small scale fire tests and cone tests indicate that the char is strengthened by the long L/D ratio of the multi wall carbon nanotubes resulting in low heat release rates.

8. Acknowledgments

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Dr. Günter Beyer joined Kabelwerk Eupen AG in 1984 and is responsible for the fire tests, material developments and qualification of new materials. He gained his PhD at the university RWTH Aachen / Germany in 1984 and has published more than 80 scientific papers mainly in the field of material science and flame retardancy of polymers. He has been invited for plenary presentations and as chairman on many international conferences. His main research interest for the moment is related to nano-structured flame retardants.

In 2003 he received an award by the IWCS organizers for his presentation on nanocomposites at the International Wire & Cable Symposium IWCS 2002:

" Outstanding Technical Paper award for the 51st Symposium. It was selected from amongst the entire Symposium as the best technical paper on the basis of technical advancement and innovation ..."

More about his research activities on nanocomposites and a full list of his publications are available at http://www.eupen.com