How Carbon Nanotube Crushing can Improve Flame Retardant Behaviour in Polymer Nanocomposites?[a]

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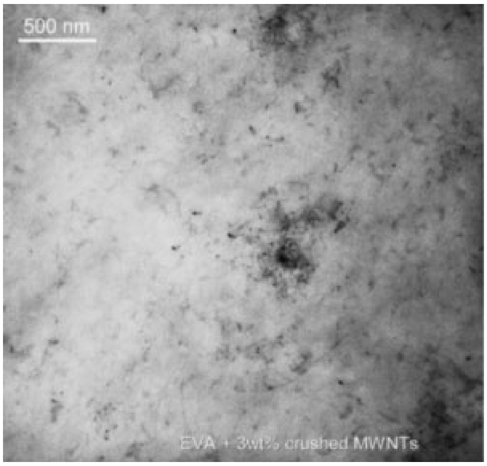
Nanocomposites based on an ethylene–vinyl acetate copolymer (27 wt.-% vinyl acetate) and multiwall carbon nanotubes (MWNTs) have been prepared by melt blending and their thermal degradation and flame retardant properties have been evaluated. Special attention has been paid to the influence of the nanotube nature on the flammability properties and more particularly on the time to ignition (TTI) as measured by cone calorimetry. It has been shown that there is a strong influence of the nature of carbon nanotubes on the fire behaviour of the composites, especially previous MWNTs crushing proved to substantially delay the TTI while maintaining much reduced heat release rate (HRR). Such a remarkable behaviour might be explained by the chemical reactivity of radical species present at the surface/extremities of crushed MWNTs during the combustion process.



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Introduction

Since 1991,[1] carbon nanotubes (CNTs) have been a major interest of study all over the world. A variety of properties and phenomena associated with CNTs have been investigated in the last 10 years. What makes nanotubes so special is their combination of dimension, structure and topology that translates into a whole range of superior properties.[2,3] One of the major challenges is actually to disperse easily and homogeneously these nanotubes in a panel of polymer matrices to obtain materials with increased properties for different application uses. Recently, it appears interesting to use CNTs at a low loading content to obtain materials with reduced flammability.[4–6]

Ethylene–vinyl acetate (EVA) copolymer is commonly used in cable industry. It is required to introduce high

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contents of fire retardant (FR) systems, such as alumina trihydrate (ATH) or magnesium hydroxide (MH), to avoid fire hazards and reduce flammability. But this high mineral loading results in a decrease of the mechanical performance of the materials.[7] Therefore, in order to obtain a set of competitive properties, it becomes interesting to enhance the efficiency of the hydrated minerals by partially substituting them with synergistic additives. Recently, great interest has been found in the partial substitution of ATH or MH by organomodified montmorillonites (oMMT) nanoparticles.[8–10]

The present work aims at reporting some key results on the fire behaviour of polymer nanocomposites based on CNTs, especially crushed multiwall carbon nanotubes (MWNTs) dispersed in EVA by conventional melt processing. The fire properties have been evaluated by cone calorimetry. Currently, only limited studies on the flammability of polymer–CNTs nanocomposites have been published[4,5] and to the best of our knowledge, no mechanism has been proposed yet to explain the improvement of the flame retardant properties of EVA–MWNTs nanocomposites, contrary to the more intensively investigated EVA–clay nanocomposites.[11]

This work will demonstrate the remarkable and actually unexpected flame retardant efficiency of EVA/crushed MWNTs nanocomposites and aims to propose a mechanism explaining the remarkable action of nanotube crushing on the substantial delay of the time to ignition (TTI) as recorded by cone calorimetry.

Experimental Part

A commercial EVA copolymer from ExxonMobil (Escorene UL00328) containing 27 wt.-% of vinyl acetate was studied. Firstly, for the sake of comparison, Cloisite® 30B, a commercial clay (montmorillonite) organo-modified by 20.3 wt.-% of bis(2-hydroxylethyl)methyl tallowalkyl ammonium cation (Southern Clay Products, USA) which is known to promote good fire resistance properties in EVA[12,13] has been used as well. The multiwall nanotubes (MWNTs) studied in this work were produced at the Nuclear Magnetic Resonance Laboratory (FUNDP, Belgium) by catalytic decomposition of acetylene on transition metal particles (Co, Fe) supported on Al_2O_3[9] and were purified after dissolution of the support in boiling concentrated sodium hydroxide–water solution and dissolution of the catalysts in concentrated hydrochloric acid–water solution. These MWNTs are characterized by an average inner diameter of 5 nm and an average outer diameter of 15 nm, corresponding to ca. 14–15 concentric layers. The average length is ca. 20 μm.

Crushed MWNTs were obtained after ball milling process for 15 h in ambient atmosphere in a ball mill with stainless steel balls. The average length is reduced to ca. 300 nm.

The EVA-based nanocomposites were prepared in a Brabender internal mixer at 140 °C, for 12 min with a speed of 45 rpm.

Cone calorimeter tests (ISO 5660) were performed on $100 \times 100 \times 4$ mm^3 compression moulded samples placed horizontally with a flux of 35 kW · m^{-2}. The results presented in this study correspond to mean values obtained from three experiments for each formulation, for which a typical variation of 10% was observed. Thermogravimetric analysis (TGA) was performed using a TA instruments Hi- Res analyser. Samples were heated under air atmosphere (74 mL · min^{-1}, Pt pan) to study the thermo-oxidative degradation, using samples of typically 15 mg, submitted to a temperature ramp from 25 to 700 °C at a heating rate of 5 K · min^{-1}.

A solution of DPPH in methanol with a concentration of 50×10^{-6} M has been prepared and 5 mL of this solution was added into tubes containing 1.5 mg of each type of MWNTs.

Results and Discussion

The cone calorimeter is one of the most effective methods for studying the flammability properties of materials. Heat release rate (HRR), in particular the peak HRR, has been found to be an important parameter to evaluate fire safety.[14] The evolution of the TTI will also be discussed in this study.

The cone calorimeter experimental results for EVA and the corresponding nanocomposites filled with 3 wt.-% of Cloisite® 30B, MWNTs and crushed MWNTs as prepared by simple melt blending are presented in Figure 1 and Table 1.

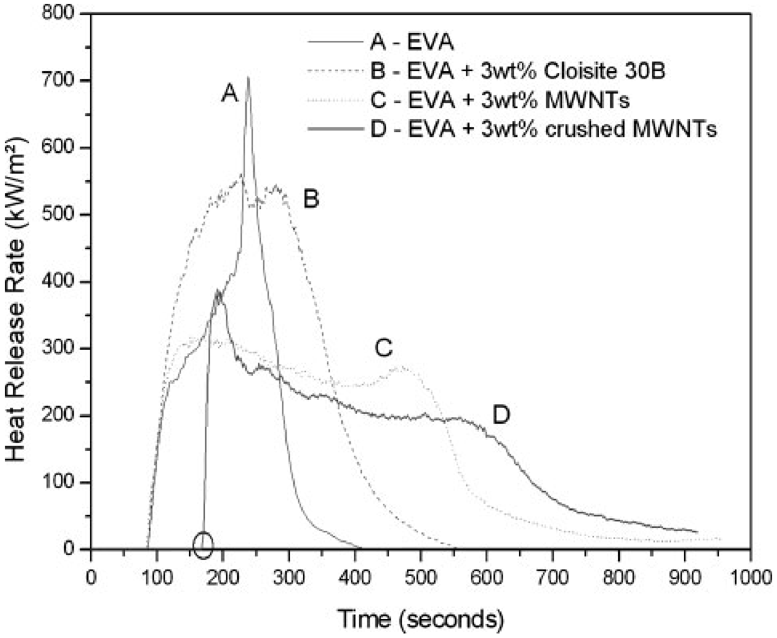

Figure 1. Cone calorimeter experiments, HRR versus time curves: comparison of the effect of the different nanofillers (Cloisite® 30B, MWNTs and crushed MWNTs).

Table 1. (TTI and maximum peak of HRR (HRR peak) as measured by cone calorimetry (35 kW · m^{-2}) for pure EVA and binary nanocompositions.

Formulation	**TTI**	**HRR peak**
	s	**kW · m^{-2}**
EVA	91	707
EVA + 3 wt.-% Cloisite® 30B	80	550
EVA + 3 wt.-% MWNTs	84	315
EVA + 3 wt.-% crushed MWNTs	170	385

The behaviour of unfilled EVA is typical of noncharring thermoplastics. The peak HRR reaches a value around 700 kW · m^{-2} and the combustion is complete after 300 s. The sample shows very strong bubbling during the combustion.

For EVA–Cloisite®30B samples, the behaviour is different. In spite of the excellent nanodispersion of this organoclay in EVA as demonstrated by XRD and TEM analyses elsewhere,[15] only slightly lower maximum value of HRR are obtained (≈500 kW · m^{-2}) and the combustion time is more extended (450 s). A protective layer is formed during the test which reduces the HRR, but this crust quickly breaks and generates a foam-like structure.

A slightly different behaviour was observed when MWNTs and crushed MWNTs are used. In spite of a different dispersion state (see supplementary information), these two types of MWNTs present a similar fire behaviour. The maximum of HRR decreases (≈300 and 380 kW · m^{-2}, respectively) and the combustion time increases for the two types of CNTs (≈700 and 900 s, respectively). The rigid crust formed in the two cases has different properties compared to the crust observed with the clay-based nanocomposite, it becomes denser and does not form a foam.

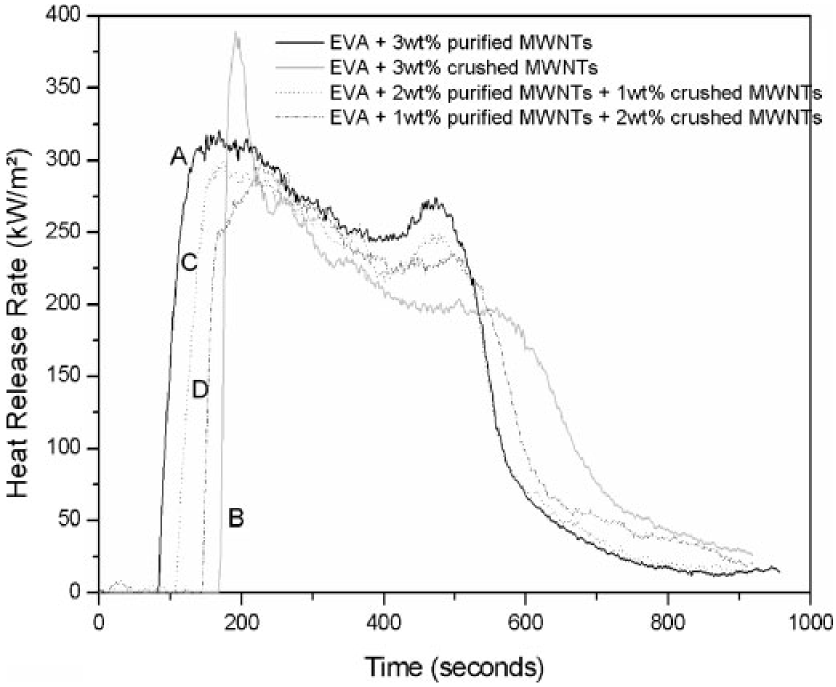

Figure 2. Cone calorimeter experiments, HRR versus time curves: comparison of the effect of the content of crushed MWNTs in the composite.

Interestingly enough, TTI is also affected by the presence of the different particles. TTI is much longer for the formulation containing crushed MWNTs, in comparison with the other composites. The effect of the organomodified clay (Cloisite®30B) on the TTI of EVA is well known and has been attributed to the catalytic effect of the acidic sites of the layered silicates that increase the rate of EVA deacetylation.[13] Other authors attribute a general trend for clay-based nanocomposites to exhibit a lower TTI due to the thermal instability (Hoffman's degradation) of the ammonium cations that commonly organomodify the clay.[12]

The slight decrease of the TTI for the composite based on MWNTs in comparison with the EVA matrix is probably due to the presence of acidic functions formed on the surface of MWNTs during the purification method (see *Experimental Part*)[9] that might slightly catalyse the EVA deacetylation as well. In sharp contrast, in spite of a similar melt viscosity (see Supplementary Information), the addition of 3 wt.-% of MWNTs previously crushed down leads to a substantial improvement of the resistance to inflammation by ca. 85 s, the period of ignition being therefore almost doubled. Interestingly, this phenomenon is moreover perfectly reproducible. In order to further confirm this effect, two ternary formulations based on various amounts of MWNTs and crushed MWNTs have been prepared and tested with the cone calorimeter. The HRR curves of these composites are presented in Figure 2 and the values of the cone calorimetry tests are summarized in Table 2. When MWNTs are partially replaced by crushed MWNTs, TTI increases with the relative amount of crushed MWNTs in the composite.

In order to understand the effect of the nanotubes crushing on TTI, the thermal decomposition by TGA recorded under air atmosphere has been studied. Different EVA-based nanocomposites filled with various relative amounts of MWNTs and crushed MWNTs have been analysed. One can observe in Figure 3 that the partial substitution of MWNTs by crushed MWNTs limits the

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Table 2. TTI and maximum peak of HRR (HRR peak) as measured by cone calorimeter (35 $kW \cdot m^{-2}$) for ternary formulations.

Formulation	TTI	HRR peak
	s	$kW \cdot m^{-2}$
EVA + 3 wt.-% MWNTs	84	320
EVA + 2 wt.-% MWNTs + 1 wt.-% crushed MWNTs	107	290
EVA + 1 wt.-% MWNTs + 2 wt.-% crushed MWNTs	155	300
EVA + 3 wt.-% crushed MWNTs	170	380

production of organic volatile compounds during the first step of the decomposition. The second step of the thermodegradation is shifted towards higher temperature, showing also the formation of more thermally stable char at 500 °C.

In order to explain this unexpected behaviour, we suggest the occurrence of chemical reactions between the EVA thermo-oxidation products and radical or radical promoting species located on the crushed MWNTs surface, which could be formed during the crushing process in the ball mill. Interestingly, the presence of a significant amount of radicals or radical promoters on the surface of crushed MWNTs has been clearly evidenced by chemical reaction with 2,2-diphenyl-1-picrylhydrazyl (DPPH). DPPH is widely used to test the ability of compounds to act as free radical scavengers or radical hydrogen donors. In the presence of such species, DPPH turns from purple to yellow.[16] When crushed MWNTs are contacted with a DPPH solution, the supernatant turns from purple to yellow, while no evolution of the DPPH purple colour is observed when it is added onto (noncrushed) MWNTs (Figure 4).

Taking into account these observations, one may therefore assume that, in the cone calorimeter, it is more likely the reaction between the radicals formed at the surface of crushed MWNTs and the radicals produced during EVA thermodegradation leads to the decrease in the amount of volatile products and the delay of materials ignition.

Conclusion

MWNTs show a significant effect on the flammability properties of EVA-based composites. Two important parameters during cone calorimetry fire testing have been influenced by adding a small amount of crushed MWNTs in EVA: TTI which is largely increased and HRR, which is

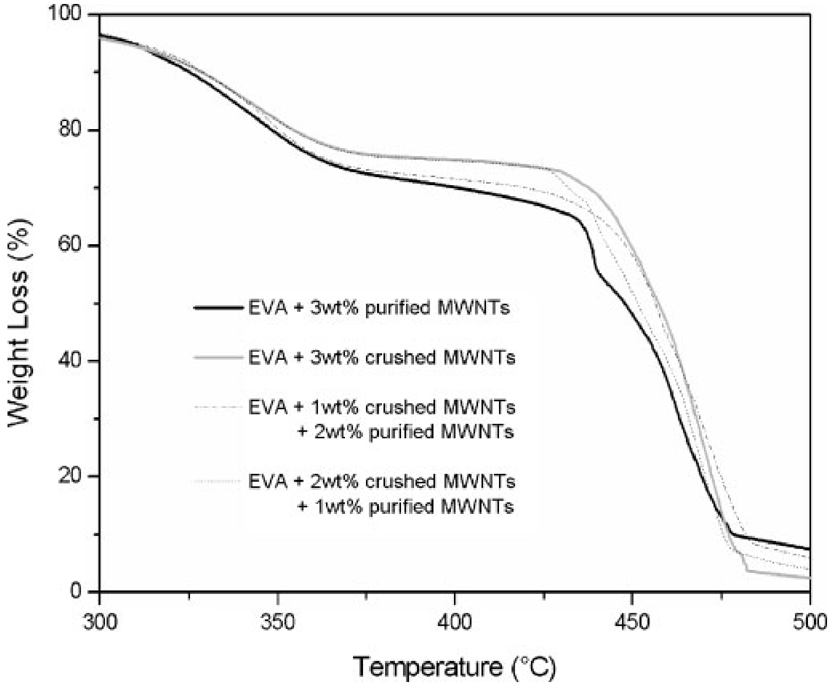

Figure 3. TGA curves of EVA-based nanocomposites: comparison of the effect of the content of crushed MWNTs.

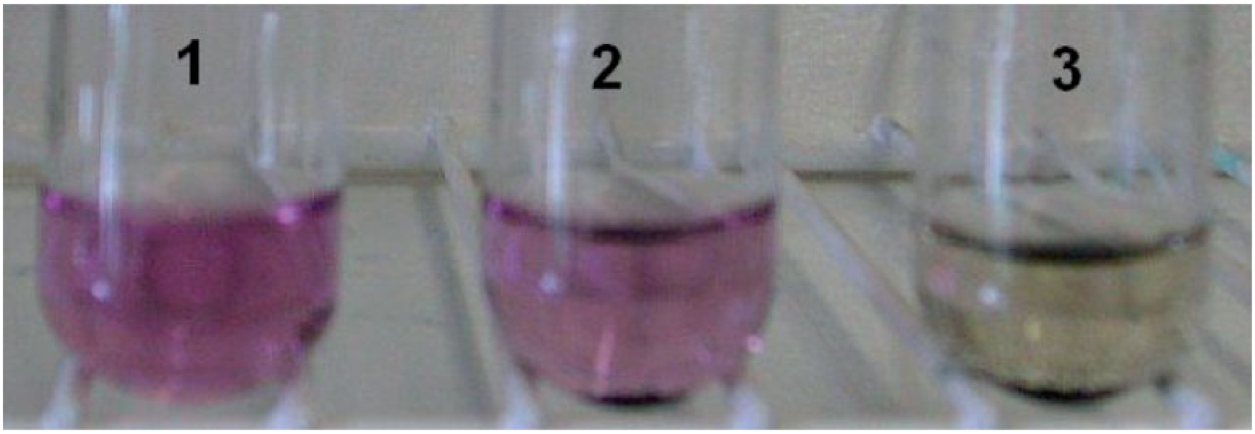

Figure 4. Qualitative assessment of the presence of radicals on the surface of crushed MWNTs. The samples are: (1) the DPPH solution alone, (2) DPPH solution in the presence of MWNTs and (3) DPPH solution in the presence of crushed MWNTs.

significantly decreased. This phenomenon can be attributed to a chemical effect through the chemical reactivity of the radical species existing at the surface of crushed MWNTs during combustion. This unique behaviour demonstrates the possibility to delay both the ignition time and reduce the flammability (HRR) of a polymer matrix like EVA by adding a small amount (a few percent) of CNTs previously crushed down by a technique as simple as ball milling.

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