MWNT Surface Self-Assembling in Fire Retardant Polyethylene-Carbon nanotubes nanocomposites

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Abstract: Multiwall carbon nanotubes (MWNT) were melt blended at different concentration with linear low density polyethylene (LLDPE). The nanotubes impart the fire-retardant characteristics to the polymer by formation of a thin protective film of MWNT/carbon char generated on the surface of the nanocomposites. The film formation mechanism is discussed.

Introduction

Carbon nanotubes (CNT) were discovered in 1976 by Endo et al. [1]. Since elucidation of the structure by Iijima in 1991 [2] CNT were widely studied for their exceptional mechanical properties [3,4,5] but also for their electrical [6] and thermal conductivity [7] . However there are also many disadvantages in their use: the difficulty to obtain homogeneous dispersion of CNT in the polymeric matrices and to transfer the strain resistance from the CNT to the final material for poor interface adhesion [8,9]. Because of the increase of production capacity in the last years the cost of MWNT decreased by a factor 10-100. In the next years carbon nanofibers and multy walls nanotubes (MWNT) will meet price barriers for most applications and will start seriously competing with current technologies.

Many nanofillers are used to reduce flammability properties for polymeric materials. At the moment the most common fire retardant approach based on nanocomposites involves the use of layered silicates having a high aspect ratio [10,11,12]. However other nanofillers such as polyhedral oligomeric silsesquioxane (POSS) [13,14] and CNT are already used. There are some works where good results were obtained using these nanofillers in combination, in order to obtain a synergic effect[15,16]. There is a number of reports [17,18,19,20,21,22] that discuss structural, spectroscopic and combustion behaviour results of CNTs-polymer systems respectively.

Fire retardance of polypropylene/MWNT nanocomposites was studied by Kashiwagi et al. [17,18] who observed that during burning a nanotubes network layer is formed which acts insulating the PP from the external radiant flux changing the transmission

of heat from thermal conduction to radiative transfer. The nanotubes layer becomes a physical shield decreasing external heat flux by one half.

Schartel et al obtained the same conclusions with polyamide-6 /MWNT nanocomposites [20]. He also reported the formation of MWNT interconnected network structure during burning so that the melt viscosity of the nanocomposite goes up and can prevent dripping and flowing.

Kashiwagi et al. [19] studied also the effect of single wall CNT dispersion on fire retardant properties for polymethyl methacrylates evidencing a direct correlation with the formation of an analogous thermal protective layer as a function of nanotubes dispersion in the polymer matrix.

Similar results were obtained by Bourbigot et al.[21] who report a decrease of mass loss rate during radiative gasification test of well dispersed MWNT-PS nanocomposite respect to sample containing MWNT roughly dispersed.

Thermal shielding could explain fire retardance contribution of CNTs but fails to interpret the delay reported [17] of CNT-polymer thermal oxidation which rate is controlled by oxygen radical initiation. In some studies [23,24] free radical scavenger effect of CNT was considered as the main reason for increasing PE thermal oxidation stability. However surprisingly the stabilisation was found to be independent from concentration and no investigation on the surface evolution of the oxidised samples were made.

In a previous article of our group on linear low density polyethylene (LLDPE)/MWNT nanocomposites [25], the oxidative degradation was examined. We find that MWNT presence delay thermal degradation under air by about $100 °C$. The results are quite independent of MWNT concentration: the stabilisation was proved to be due to formation of a thin protective film of MWNT/carbon char generated on the surface of the nanocomposites.

In the present work, in order to investigate the relevance of this mechanism on fire retardance properties, the same LLDPE/MWNT nanocomposites were tested under forced-flame conditions. Polyethylene-MWNT nanocomposites at different CNTs loadings were studied. Both crude and purified MWNT are used here to assess whether impurities play a role on thermal oxidation and combustion behaviour of CNTs based polymer nanocomposites.
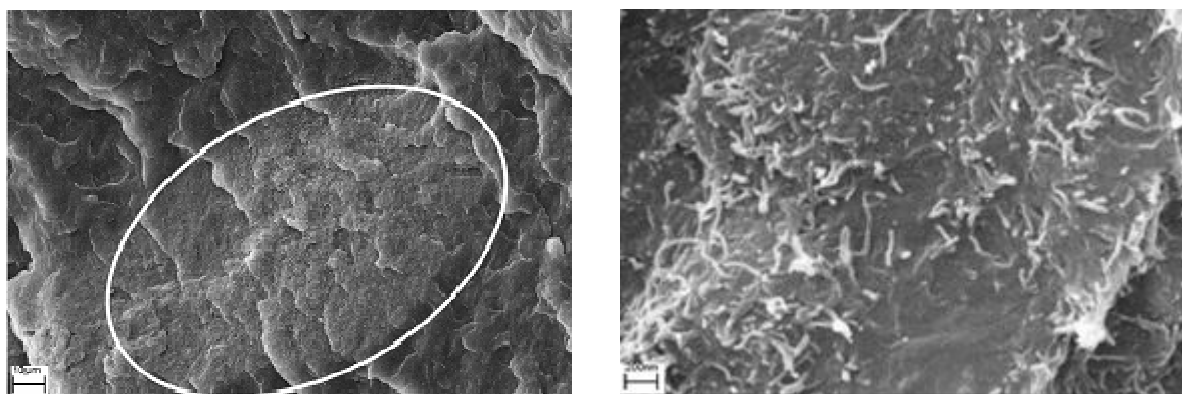
Results and Discussion

Fig. 1. SEM micrograph of PE1, a) MWNT dispersed inside LLDPE (encircled area) 10 µm size mark b) magnification of encircled area 200 nm size mark

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The morphological study was made in details in a previous paper [25]. The structure of the nanocomposites (Fig. 1) shows quite a good dispersion of the MWNT inside the matrix but a poor distribution because of the entanglements that prevent homogeneous dispersion of the single carbon nanotubes.

Cone calorimeter describes the behaviour of materials combustion simulating different fire conditions. The 50 kW m^{-2} radiant heat from cone heater used here corresponds to a well-developed fire.

Virgin LLDPE samples in the cone calorimeter begin to burn after melting, producing an evident bubbling. The combustion parameters are listed in Tab. 1.

Tab. 1. Cone calorimeter of melt-blended samples: time to ignition (TTI), peak of heat release rate (pkHRR), total heat release (THR), total carbon monoxide (TCO), total carbon dioxide (TCO2), Total Smoke Release (TSR), Fire Performance Index (FPI), FIre Growth Rate index (FIGRA).

Sample		PE	PE05	PE09P	PE1	PE3
TTI	s	51 ± 3	35 ± 1	43 ± 2	42 ± 2	45 ± 4
pkHRR	Kw m^{-2}	1290 ± 60	780 ± 10	720 ± 20	670 ± 20	750 ± 40
THR	MJ m^{-2}	116 ± 2	111 ± 2	112 ± 1	112 ± 2	114 ± 2
TSR	m^2 m^{-2}	1130 ± 110	1414 ± 53	1582 ± 90	1481 ± 33	1503 ± 69
TCO	mg/g	31 ± 2	31 ± 1	32 ± 1	32 ± 1	33 ± 2
TCO2	g/g	3.27 ± 0.02	3.12± 0.04	3.01 ± 0.06	3.12± 0.04	3.05 ± 0.03
FPI	kW m^2 s^{-1}	25 ± 3	22 ± 1	17 ± 1	16 ± 1	17 ± 2
FIGRA	kW m^{-2} s^{-1}	10.4 ± 0.5	7.9 ± 0.2	6.1 ± 0.3	6.2 ± 0.3	6.9 ± 0.4

MWNT presence modifies the combustion of the nanocomposites as compared to LLDPE. All the nanocomposite samples burn without bubbling. The surface of burning nanocomposite specimens evolves forming a char that swells because it is blown by gases generated by the decomposing polymer matrix.

The time to ignition (TTI) of nanocomposites in the cone calorimeter combustion is shorter than for LLDPE and increases with MWNT concentration. Kashiwagi et al [18] supposed this behaviour be the result of antagonist effects: the radiant heat absorbed from cone heater by the nanocomposites is higher than the heat absorbed by LLDPE because of the black colour and independent from MWNT concentration; in contrast, the increase of MWNT concentration increases nanocomposite thermal conductivity, which leads to distribution of heat from cone on a larger volume of material thus delaying the degradation which supplies combustible volatiles for ignition.

The peak of HRR (pkHRR)and the total heat release (THR) are two of the most important fire behaviour characteristics, corresponding to total fire load and flame spread respectively. Peak of HRR is about 55 % of original value for LLDPE on the other hand the total heat release is similar for MWNT nanocomposites and LLDPE. It can be deduced that the presence of MWNT does not decrease the quantity of polymer burned: but it slows considerably its combustion. The quantity of carbon monoxide and dioxide produced (TCO and TCO2) is similar for the MWNT nanocomposites and LLDPE, it confirms the effect of MWNT only on the combustion rate.

The presence of MWNT increases instead the quantity of smoke produced that is one of the important risk factor during fire. The total smoke release (TSR) is increase of about 30 % for all concentrations of MWNT.

The HRR curves do not show major differences on increasing the concentration of MWNT in the nanocomposites (0.5-3 %wt) (Fig. 2).
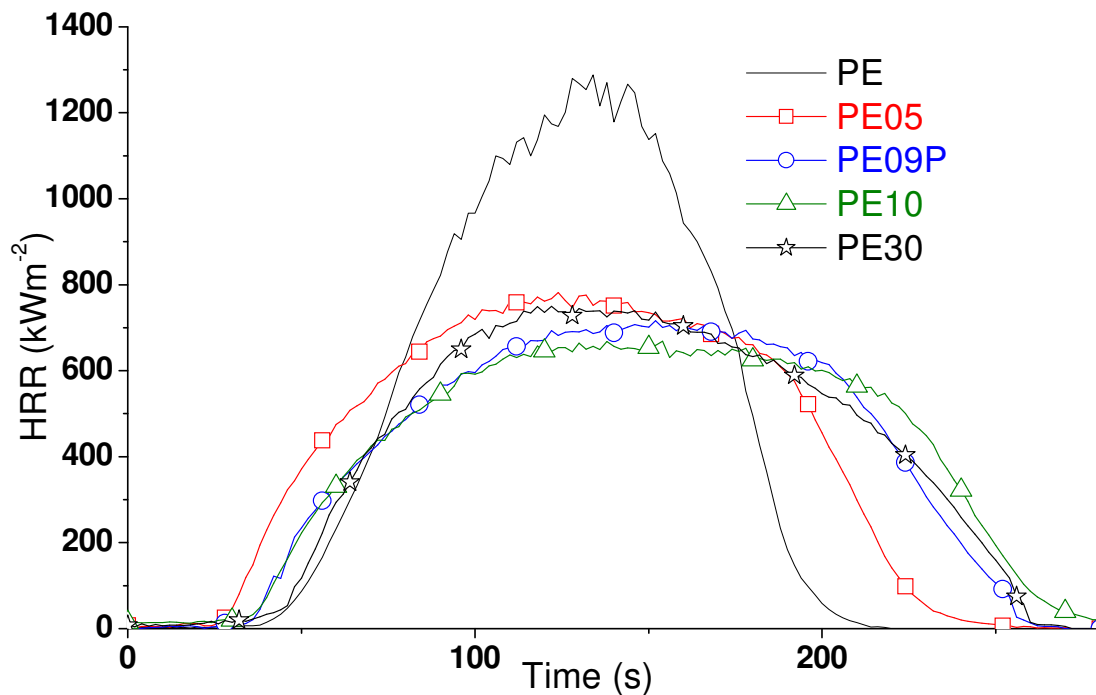

Fig. 2. Heat release rate (HRR) plotted against time, heat flux 50 kW m^{-2}

The Fire Performance Index (FPI) is defined as the peak of HRR divided by the TTI. It is a empirical index suggested to be related to the time to flash-over i.e. change from small to large-scale fire (or time available for escape) in a real fire. Thus it may be considered to be the best individual indicator of overall fire hazard [26]. Lower values of FPI indicate less fire hazard. The FPI decreases by 12 % at 0.5 %wt MWNT loading and by 30 %wt from and above 1.0 %wt loading showing an improve of the overall fire retardance of composites. Similar results were obtained using FIGRA, an index originally used for the single burning item evaluation of fire spread that indicates the spread of fire, in our case the nanocomposites show a lower spread rate than pure LLDPE.

The combustion residues change decreasing the concentration of MWNT from a well-compact structure to isolated islands (Fig. 3). During burning these structures are covered by a reflective black film which collapses at the end of combustion, forming the final structure of the residues. This phenomenon is more evident at low concentration of MWNT. The film is formed by MWNT and a carbon char that is grown on them (Fig. 4).

The internal structure of the residues seen with SEM is similar for all the samples and shows the formation of a dense porous structure practically homogeneous at nanometric level (Fig. 5) where individual nanotubes are strongly interconnected.
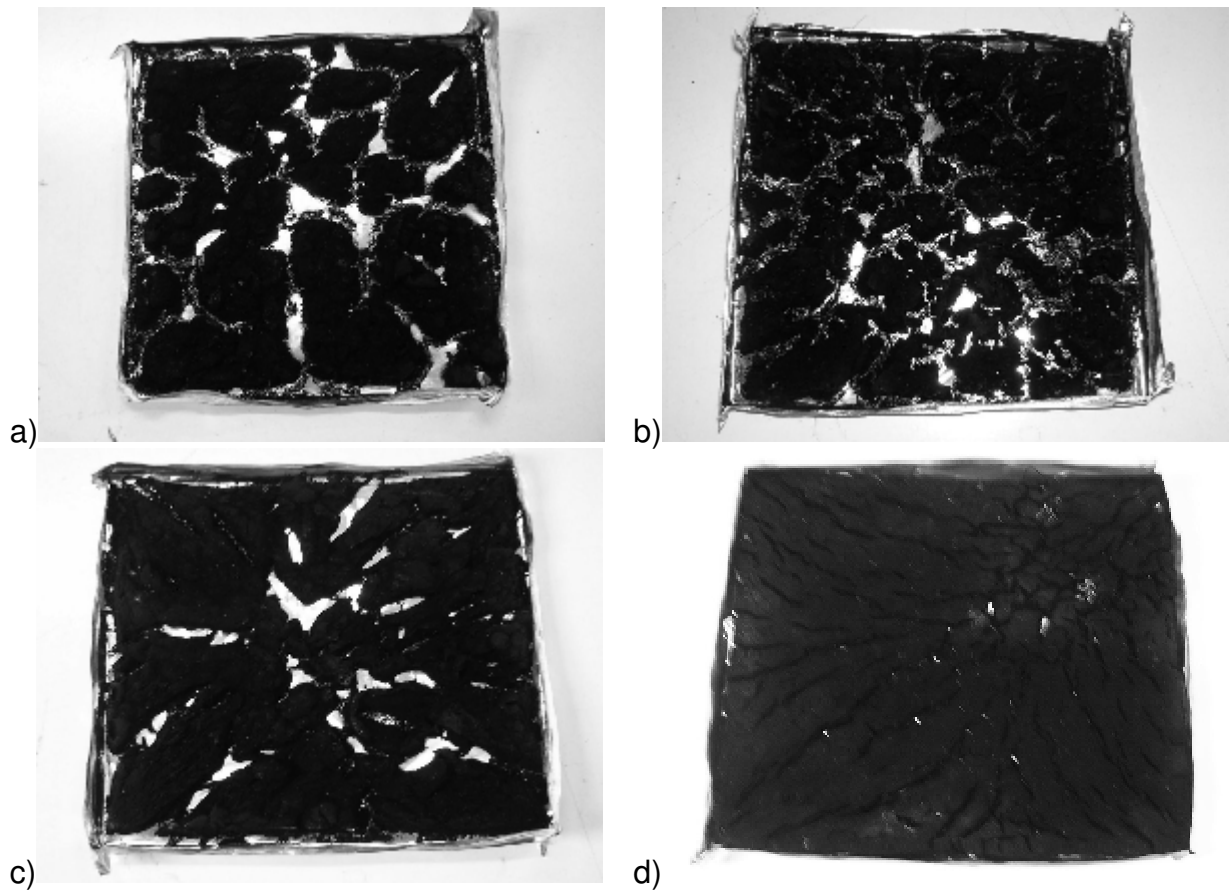
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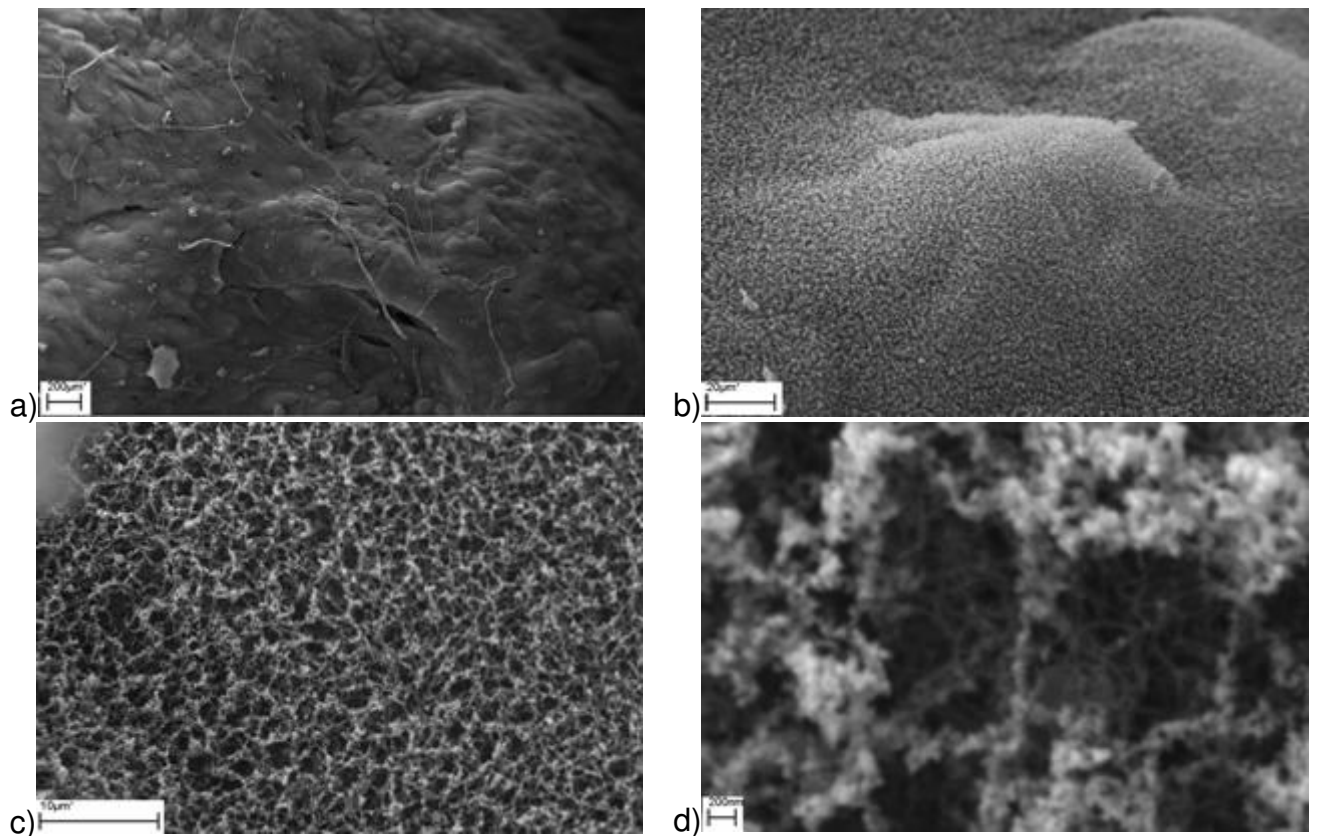**Fig. 3.** Cone residues a) PE05 b) PE09P c) PE10 d) PE30

Fig. 4. SEM analyses of the film that cover PE05 specimens during combustion.
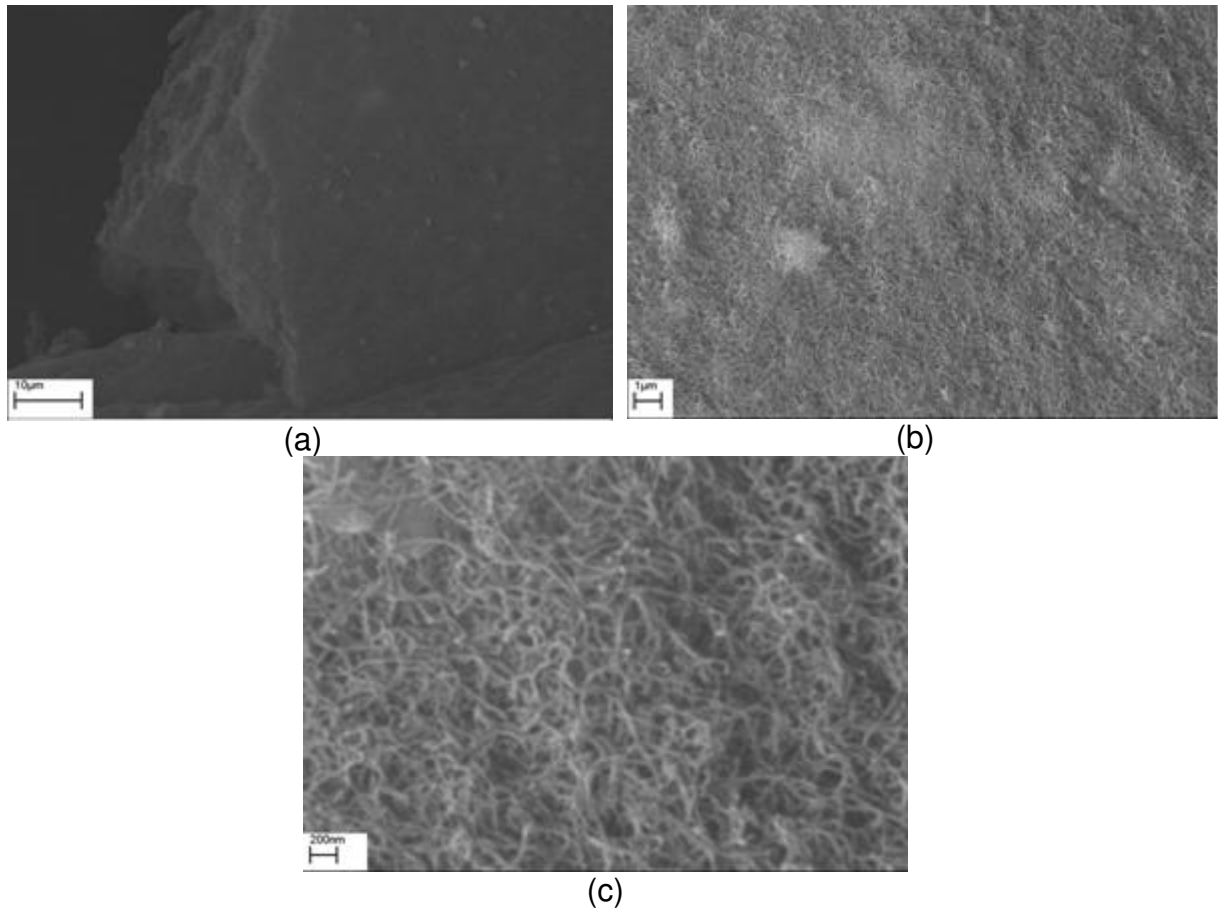
Fig. 5. SEM micrograph of PE10 cone residues a) 10 μm size mark b) 1 μm size mark c) 200 nm size mark

The MWNT original structure of separated aggregates of entangled ropes is lost inside the residue to give a continuous structure of entangled nanotubes.

A good initial dispersion and distribution are indicated for polypropylene from Kashiwaghi et al. [17,18] as the most important factors in order to increase flame retardant properties of the polymer. These authors observed that during burning a nanotube network layer is formed without evident cracks and this layer acts insulating the PP from the external radiant flux changing the transmission of heat from thermal conduction to radiative transfer. The nanotube layer becomes a physical shield decreasing external flux at less than one half of initial flux. Kashiwagi et al. [19] studied also the effect of single wall CNT dispersion on fire retardant properties for poly methyl methacrylates evidencing a direct correlation between an homogenous distribution, the formation of a continuous layer and the fire-retardant effect.

An homogeneous distribution is apparently not critical from our data as far as combustion in cone calorimeter is concerned. Whereas in the literature it is generally found that the effectiveness of fire retardants acting by creation of a protective surface on the polymer material increases when the surface coating is continuous, in our case it is independent of the presence of cracks in the protective surface layer. Indeed a similar HRR was found for nanocomposites with low MWNT content which leave an highly fragmented combustion residue (e.g. Fig. 3a MWNT 0.5%) or for nanocomposites reached in MWNT leaving a compact residue (e.g. Fig. 3d).

In a previous paper on the same nanocomposites the stabilisation in thermal oxidation of LLDPE due to the MWNT was studied [25]. The formation of a surface polyaromatic carbon char favoured by the MWNT was reported. MWNT/char composite layer formed protects the underlying polymer from oxygen. An eventual

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protection from heat and mass transfer decreasing rate of combustion due to formation of a film on the surface of the specimens is in good agreement with independence of pkHRR of MWNT concentration. Indeed a surface effect could explain the independence from concentration, a small amount of MWNT is required: a thin protective film is rapidly formed already with the lowest MWNT concentration used here (0.5 %wt) (Fig. 4). Larger amounts of MWNT would not provide further contribution to decreasing the rate of combustion. Whereas, increasing MWNT concentration increases time to ignition: at 3 %wt concentration the negative effect due to larger radiation heat absorption of the composite as compared to virgin polymer, is overcome (Fig. 2).

This behaviour is different from what reported by Kashiwagi et al. for polypropylene (PP) [17,18]. It can be supposed that the difference is in the different stability of the nanocomposites to thermal degradation. The PP/MWNT nanocomposites result more stable than PP to thermal degradation however, on the contrary of what reported for PE/MWNT [23,24,25], only the temperature of maximum degradation rate is shifted towards higher values while there is no evidence of formation of a stable charred surface.

A mechanism for nanocomposites burning in the cone calorimeter is proposed in Fig. 6: surface polymer ablation, upon exposure to radiant heat from the cone, creates a thin surface layer rich of MWNT which protects the polymer from the heat source and hinders mass transfer.

Furthermore, this thin film is blown by the gases evolved from underlying decomposing polymer with creation of voids underneath the surface which shift the heat transfer to the specimen, from conductive to a less effective radiative mechanism. With progression of combustion, the surface film may break, but it is readily regenerated by exposure to heat of the material underneat.

Finally the increase of total smoke released might be due to limited volatilisation of the charring polymer while the surface protective char is being created. This surface, being full of aromatic compounds, oxidise only partially producing smoke.
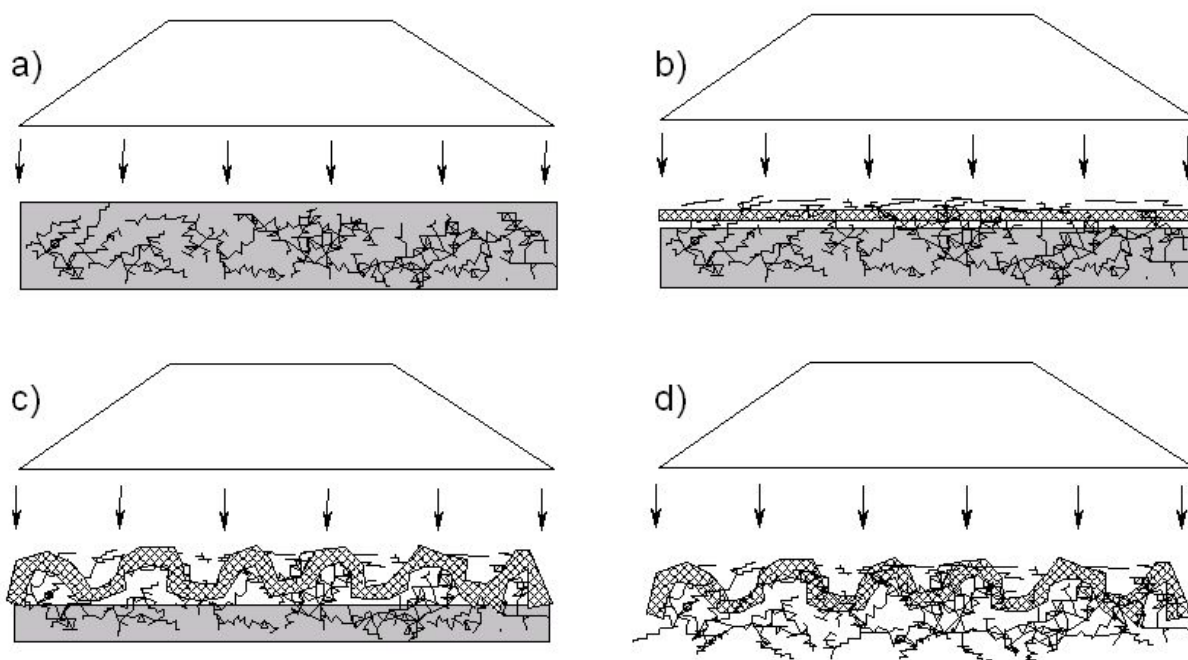
Fig. 6. Thermal protection mechanism in cone calorimeter, (a) the heat flux from cone degrades the surface LLDPE at the same temperature of pure LLDPE (b) MWNT accumulate on the surface and form a thin film which (c) tends to form bubbles insulating the material below which degrades at a lower rate than pure LLDPE leaving (d) the MWNT filler residue.

Conclusions

The MWNT dispersed in LLDPE confer fire-retardant characteristics to LLDPE. This stabilisation is, in the range studied, quite independent of concentration showing that, more than a mass effect, the stabilisation is due to a surface effect of a layer of MWNT/carbon char network formed during the first step of LLDPE volatilisation during LLDPE thermal oxidative degradation. Thus the thermal stabilisation of MWNT/LLDPE nanocomposites can be reached with relative low concentration of MWNT(0.5 %).

Experimental part

Materials

LLDPE ``Lupolex 18Q FA'' supplied by Basell was used. MWNT Nanocyl®-7000 and purified MWNT (PMWNT) produced by removing aluminium oxide by acid solution Nanocyl®-3100 supplied by Nanocyl were used, properties are summarized in Tab. 2.

Tab. 2. MWNT description.

Property (Unit)	MWNT	PMWNT
Average diameter (nm)	10	10
Length (μm)	0.1-10	0.1-10
Carbon purity (%)	90	> 95
Metal oxides (Al_2O_3) (%)	10	<5

The nanocomposites were prepared via melt-blending using an internal mixer as previously reported in detail [25]. Percent MWNT content is indicated by the sample name (e.g. PE05 contains 0.5 %wt MWNT) as reported in Tab. 3. A sample has been prepared with 0.9 %wt of purified MWNT (PMWNT) (PE09P). Specimens for cone calorimeter were prepared by hot pressing using a hydraulic press with the two plates heated at 140°C using a pressure of 25 bar for 5 minutes.

Tab. 3. Composition of melt-blended samples and abbreviations of the materials.

Sample	LLDPE %wt	PMWNT %wt	MWNT %wt
PE	100.0	0.0	0.0
PE05	99.5	0.0	0.5
PE09P	99.1	0.9	0.0
PE1	99.0	0.0	1.0
PE3	97.0	0.0	3.0

Scanning electron microscopy (SEM)

Morphology was examined using a SEM apparatus LEO 1450 VP equipped with energy dispersive spectroscopy (EDS). Samples were fractured after cooling by immersion in liquid nitrogen. Samples from cone calorimeter were directly used.

Oxygen consumption calorimetry (Cone Calorimeter)

The cone calorimeter tests were performed according to the ISO 5660-1 standard using a Fire Testing Technology Standard Cone Calorimeter; the samples (100x100x3 mm) were irradiated with a 50 kW m^{-2} heat flux and the ignition of the flame was obtained by a spark.

The combustion behaviour is evaluated by: time to ignition (TTI), heat release rate (HRR), peak of heat release rate (pkHRR), fire performance index FPI (defined as pkHRR/TTI), total heat release (THR), total smoke release (TSR), total evolution of CO (TCO) and CO_2 (TCO2) for weight of initial sample (weight of CO_X evolved divided for initial weight of sample). To analyse fire spread, analogously to ``Single Burning Item''(EN 13823:2002), a FIGRA (FIre Growth RAte) index is defined as maximum of the ratio of HRR respect to time. The reported results are average of at least 3 measurements.

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