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Polymer Degradation and Stability 92 (2007) 1873–1882

Polymer Degradation and Stability

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Polymer/carbon nanotube nanocomposites: Influence of carbon nanotubes on EVA photodegradation

Sandrine Morlat-Therias [a,*], Elisabeth Fanton [a], Jean-Luc Gardette [a], Sophie Peeterbroeck [b], Michael Alexandre [b], Philippe Dubois [b]

[a] *Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS-UBP 6505, Université Blaise Pascal (Clermont-Ferrand), F-63177 Aubiere Cedex, France*

[b] *Centre d'Innovation et de Recherche en Matériaux Polymères (CIRMAP), Service des Matériaux Polymères et Composites, Materia Nova asbl – Université de Mons-Hainaut, Place du Parc 20, B-7000 MONS, Belgium*

Received 17 April 2007; accepted 28 June 2007
Available online 22 July 2007

Abstract

The influence of carbon nanotubes on the photodegradation of EVA/carbon nanotube nanocomposites was studied by irradiation under photooxidative conditions (at $\lambda > 300$ nm, at 60 °C and in the presence of oxygen). The influence of the nanotubes on both the photooxidation mechanism of EVA and the rates of oxidation of the matrix was characterized on the basis of infrared analysis. On one hand, it was shown that the carbon nanotubes act as inner filters and antioxidants, which contribute to reduction in the rate of photooxidation of the polymeric matrix. On the other hand, it was shown that light absorption could provoke an increase in the local temperature and then induce the photooxidation of the polymer. The competition between these three effects determines the global rate of photooxidation of the polymeric matrix. Several factors are involved, the concentration of the carbon nanotubes, the morphology of the nanotubes and the functionalization of the nanotube surface.

Keywords: Carbon nanotubes; Nanocomposites; Photooxidation; Stabilization

1. Introduction

Finely dispersing particles in polymer matrices is nowadays a widely used method that allows increasing property such as stiffness, and mechanical properties of the composite materials. Depending on the nature of the added filler, other properties such as fire resistance, thermal and electrical conduction can also been enhanced. Polymer nanocomposites represent a new class of composite materials with fillers displaying at least one dimension in the nanometer range. These nanocomposites provide materials with significantly improved properties at lower filler content (about 3–5 wt%) than that in conventional composites. The most commonly studied polymer nanocomposites are clay based, mainly with montmorillonite (MMt) as layered silicate filler [1]. Upon incorporation of organo-modified clays (organo-clays) in a polymer matrix, two nano-morphologies can be obtained, either intercalation of the polymer chain between the clay platelets keeping the stacking of the sheets, or exfoliation of the clay platelets with a disordered dispersion of the inorganic sheets in the polymer. Ethylene-vinyl acetate (EVA) copolymers appear to form such morphologies, however, complete exfoliation is difficult to achieve and semi-intercalated/semi-exfoliated nanostructures are mainly generated [2–6].

Carbon nanotubes represent another family of potential nanofillers. Carbon nanotubes, firstly described by Iijima in 1991 [7], are a new allotropic form of carbon built up of carbon atoms arranged in hexagons and pentagons, forming cylinders. Typically, carbon nanotubes consist of single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs) where several nanotubes of decreasing diameter are interlocked. These materials have potential applications in numerous fields

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[*] Corresponding author. Tel.: +33 4 73 40 71 43; fax: +33 4 73 40 77 00.
E-mail address: sandrine.therias@univ-bpclermont.fr (S. Morlat-Therias).

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doi:10.1016/j.polymdegradstab.2007.06.021

such as electrical and thermal conductivity and hydrogen storage.

The elaboration of polymer nanocomposites based on carbon nanotubes has been recently described in the literature. Homogeneous dispersion of the nanotubes in the polymer matrix is difficult to achieve and bundles of aggregated MWNTs persist most often [8]. Carbon nanotubes provide another candidate as flame retardant additive [9–12]. Improvement in flammability properties of polymers has been obtained with nanoscale additives. For instance, the effects of nanotube dispersion and concentration on the flammability properties were investigated with SWNTs and PMMA matrix [13]. Fire property measurements performed on nanocomposites based on EVA and multi-walled carbon nanotubes (MWNTs) revealed that carbon nanotubes are highly effective flame retardants [10,14].

The growing interest toward applications of nanocomposite materials in many industrial fields is the driving force for the development of new polymer matrix/nanofiller formulations. Among the tremendous literature devoted to nanocomposite materials, only very few papers [15–20] deal with the long-term ageing of polymer/clay nanocomposites, and more particularly with the UV-light photodegradation of these materials. These studies concern nanocomposites with montmorillonite and polymer matrices, such as polypropylene [15,18-20], polyethylene [16] and polycarbonate [17]. In all cases, similar conclusions are obtained, which show that the nanocomposites degrade faster than the pristine polymers. This relative instability of nanocomposites to UV-light ageing could constitute a major drawback for the applications of these materials in outdoor applications.

At first sight, this observation is quite unexpected, and for that reason, the behaviour of nanocomposites when exposed to light requires much closer attention. In previous papers published by some of us concerning the photooxidation of polypropylene/montmorillonite nanocomposites [18–20], a significant reduction in the induction period of oxidation was observed in the presence of MMt. This was explained by interactions between the organo-clays and the antioxidants. Several hypotheses were proposed in order to explain these interactions: adsorption of additives onto the clay, catalytic effect of iron impurities of the organo-montmorillonite, and degradation of the alkyl ammonium cations of MMt [20].

This paper reports on the study of the photodegradation of nanocomposites based on EVA as polymer matrix and on MWNTs as carbon nanotubes. As recalled above polymer/carbon nanotube nanocomposites exhibit improved thermal and mechanical properties as well as fire retardant behaviour. The photochemical behaviour of such nanocomposites is of prime importance as the durability is the key factor for outdoor applications. The chemical modifications resulting from photooxidation were investigated by infrared spectroscopy. The influence of carbon nanotubes on the mechanism of oxidation of the EVA matrix was evaluated. The rates of degradation of EVA/MWNTs nanocomposites were compared with pristine EVA and the influence of the filler content between 1% and 5% as well as the morphology and aspect ratio presented by different kinds of carbon nanotubes was discussed.

2. Experimental

2.1. Materials

A commercial ethylene-*co*-vinyl acetate copolymer, Escorene UL00328 (Exxon), with a content of 27 wt% of vinyl acetate, has been chosen as the soft polymeric matrix.

Two types of carbon nanotubes (NTs) have been investigated: multi-walled nanotubes (MWNTs) and double-walled carbon nanotubes (DWNTs). MWNTs were produced by CCVD, i.e., catalytic decomposition of acetylene on transition metal particles (Co, Fe) supported on Al_2O_3 [1]. The MWNT synthesis was carried out in a fixed-bed flow reactor at 700 °C for 60 min. Purified MWNTs were obtained after dissolution of the support in boiling concentrated sodium hydroxide water solution and dissolution of the catalysts in concentrated hydrochloric acid water solution. DWNTs were kindly supplied by Nanocyl S.A. (Belgium). The properties of each kind of carbon nanotubes are reported in Table 1. Three different kinds of MWNTs were studied. Thin MWNTs were also produced by adapted CCVD. Crushed MWNTs were obtained from purified MWNTs placed in a ball milling device for 15 h under air atmosphere.

2.2. Functionalized carbon nanotubes

The chemical modification and the covalent functionalization of carbon nanotubes with organic species like alcohols, amines and polymers have been recently reported. Surface-modification of MWNTs was carried out either with hydroxyl groups or with acetate groups. The –OH functionalization consists of a two-step reaction: carboxylation of MWNTs with $KMnO_4$, and reduction with DiBAlH. The acetate functions are obtained after reaction of the OH-MWNTs with acetic anhydride. The content of each kind of chemical function was determined by XPS and is equal to 1.3 and 1.1% respectively for hydroxyl and acetate functions [21].

Homogeneous surface coating of long carbon nanotubes has been achieved by in situ polymerization of ethylene which allows for the break-up of the native nanotube bundles leading then, upon melt blending with a polymeric matrix, to high-performance polyolefinic nanocomposites [22]. The PE coating is obtained by the polymerization-filling technique (PFT). PFT applied to carbon nanotubes consists in anchoring methylaluminoxane (MAO), a well-known co-catalyst used in metallocene-based olefin polymerization process onto the surface of carbon

Table 1
Properties of carbon nanotubes

Type of NTs	Impurities (wt%)	Number of sheets	Length (μm)	Diameter (nm)
Purified MWNTs	5	10–12	~10	15
Thin MWNTs	5	4–6	3–4	10
Crushed MWNTs	5	10–12	~300 nm	15
DWNTs	5	2	~2.2	2.5

nanotubes. A metallocene catalyst, i.e., bis(pentamethyl-η-5-cyclopentadienyl)zirconium (IV) dichloride ($Cp^*_2ZrCl_2$) in this study, is then reacted with the surface-activated carbon nanotubes. A methylated cationic species ($Cp^*_2ZrMe^+$) is formed upon reaction and remains immobilized at the vicinity of the nanotubes' surface by electrostatic interactions with simultaneously formed MAO counteranions fixed at the nanotubes' surface. Addition of ethylene leads to the synthesis of polyethylene (PE) exclusively at the surface of the carbon nanotubes [23].

TEM characterization of these MWNTs-PE [22,24] has shown typical single long MWNT completely separated from the starting bundle and the carbon nanotube was coated homogeneously with a thin layer of high density PE (relative content: 43 wt%).

2.3. Nanocomposite preparation

Polymer/NTs nanocomposites were prepared in a Brabender bench scale internal mixer at 140 °C, for 12 min with a speed of 45 rpm.

The compositions of the nanocomposite samples are described in Table 2.

The morphological, mechanical and rheological properties of the samples have already been described [8]. Morphological characterization by TEM and AFM showed a rather limited extent of NTs dispersion in EVA, many agglomerations were still visible forming long bundles of NTs. However, the crushed MWNTs provide a better dispersion. Longer carbon nanotubes, e.g. purified MWNTs, might trigger a higher degree of interconnectivity that leads to a significant reduction of the nanofiller dispersion.

The samples were compression-moulded in the form of films (thickness < 50 μm) between PTFE films at 200 bar for 1 min at 120 °C. Films with thickness under 50 μm are required in order to allow IR analysis by transmission despite the high absorption resulting from the presence of black carbon nanotubes.

2.4. Irradiation and characterization

Irradiations at $\lambda > 300$ nm in presence of oxygen were carried out in a SEPAP 12/24 unit at a temperature of 60 °C. This apparatus is designed for the study of polymer photodegradation in artificial conditions corresponding to a medium acceleration of ageing [25]. SEPAP 12/24 units are equipped with four medium pressure mercury lamps. A borosilicate envelope filters the UV-light with wavelengths below 300 nm.

Infrared spectra were recorded with a Nicolet 5SX-FTIR spectrometer, working with OMNIC software. Spectra were obtained using 32 scans and a 4 cm^{-1} resolution. In order to compare the spectra of different formulations of nanocomposites, a calibration accounting for the small variations of thickness (e, in μm) and the relative EVA content of each sample was performed using the band at 720 cm^{-1} (ν(C–H) characteristic vibration of a stretching band of PE).

Table 2
Composition of EVA/NTs nanocomposites

Samples	NTs (wt%)	Type of NTs
EVA/MWNTs(1)	1	Purified MWNTs
EVA/MWNTs(3)	3	Purified MWNTs
EVA/MWNTs(5)	*5*	*Purified MWNTs*
EVA/cMWNTs	3	Crushed MWNT
EVA/tMWNTs	3	Thin MWNT
EVA/DWNTs	*5*	*DWNTs*
EVA/MWNTs-OH	3	MWNTs-OH
EVA/MWNTs-acetate	3	MWNTs-acetate
EVA/MWNTs-PE	3	MWNTs coated with PE

3. Results and discussion

3.1. Photooxidation of EVA

3.1.1. Infrared analysis

The IR spectrum of a pristine EVA film with 28% VA (EVA 28) is presented in Fig. 1 and the main spectral features of an EVA polymer are given in Table 3.

UV-light irradiation of EVA produces notable modifications of the IR spectra (Fig. 1). A broad band develops in the hydroxyl domain (Fig. 1b) with absorption maximum at 3520 cm^{-1} and an absorption band appears as a shoulder of the VA band in the carbonyl domain (Fig. 1a). A careful examination of the modifications in the carbonyl domain on subtracted spectra (Fig. 1c) reveals that this shoulder can be characterized by a maximum at 1718 cm^{-1} and a weak band at 1780 cm^{-1} (Fig. 1c), which both develops next to the main absorption band of the acetate function at 1740 cm^{-1}. Moreover, several absorption bands appear with maxima at 909 cm^{-1}, and also at 990 cm^{-1} and 960 cm^{-1} (Fig. 1d).

In a previous study of the photooxidation of EVA [26,27], these IR absorption bands have been attributed to the formation of carboxylic acid functions at 1718 cm^{-1}, of lactone at 1780 cm^{-1}, and unsaturations corresponding to vinyl bonds ($-CH{=}CH_2$) at 909 cm^{-1} and 990 cm^{-1} and to vinylene bonds ($-CH{=}CH-$) at 960 cm^{-1}. The increase of absorbance at 3520 cm^{-1} in the hydroxyl domain was attributed to alcohols associated with acetate groups.

3.1.2. Mechanism

In photooxidative conditions, under UV-light irradiation at wavelengths above 300 nm, the degradation of nonchromophoric polymers is likely to be initiated by chromophoric impurities which absorb UV-light and produce radicals that further react with the polymer [28]. The mechanisms of oxidation that have been proposed [26] can be summarized as following in Scheme 1.

Hydrogen abstraction on the polymeric backbone either on a methylene group (in PE sequences), or on a tertiary carbon atom in α-position of the acetate function produces macroradicals. These radicals are known to react with oxygen, leading to a peroxy radical that gives a hydroperoxide by abstraction of a labile hydrogen atom. The alkoxy radical A formed on

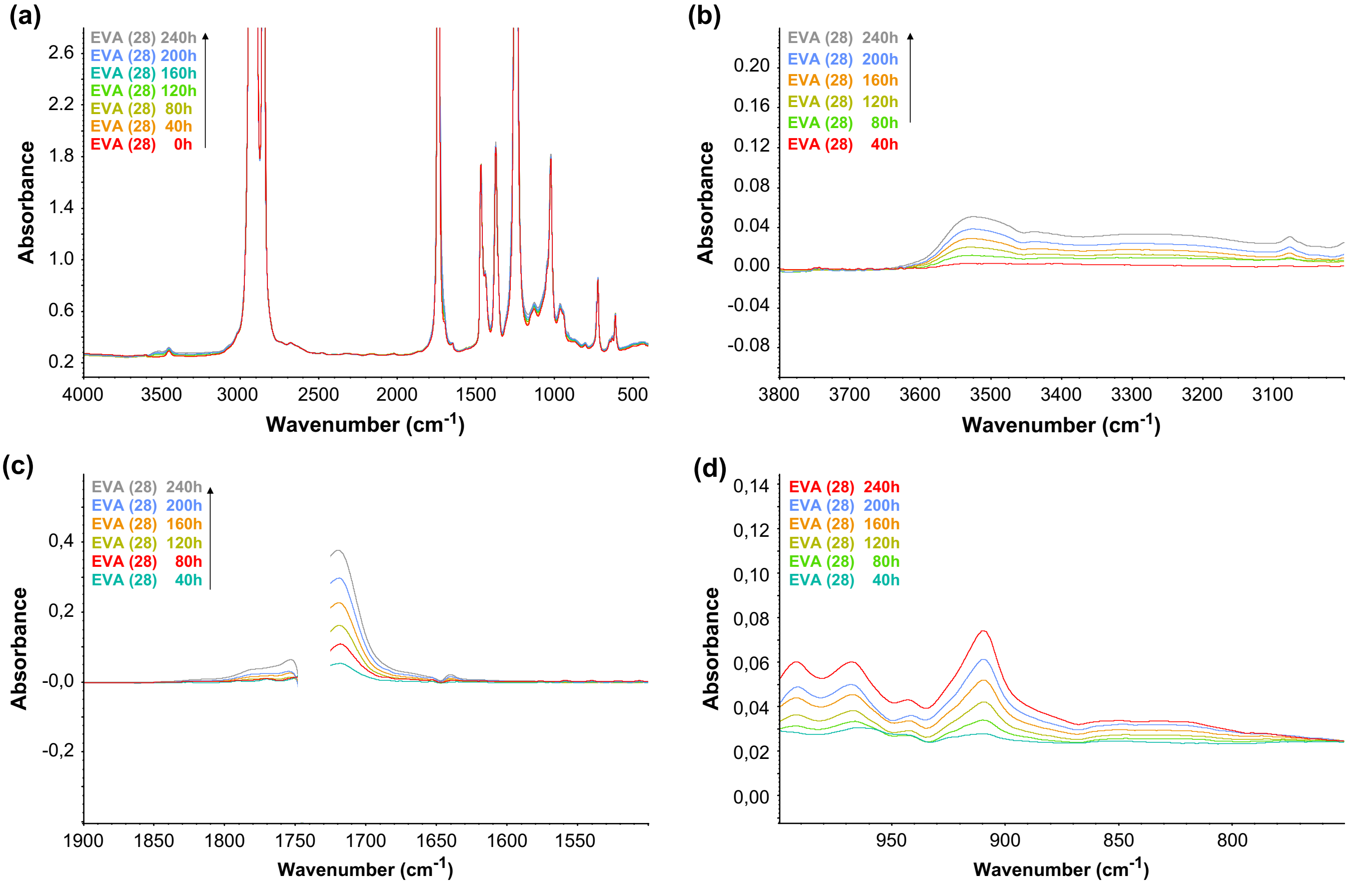


Fig. 1. FTIR spectra of an EVA (28) film photooxidised at $\lambda > 300$ nm, 60 °C; (a) direct spectra in the domain 4000–400 cm^{-1}; (b) subtracted spectra (Ft – F0) in the domain 3800–3000 cm^{-1}; (c) subtracted spectra (Ft – F0) in the domain 1900–1500 cm^{-1}; (d) subtracted spectra (Ft – F0) in the domain 1000–750 cm^{-1}.

PE sequences leads to the formation of alcohol or ketone. The oxidation of the tertiary carbon atoms B leads only to the formation of ketone, no alcohols being obtained from this route. Both routes of oxidation lead to similar chain ketones. Photolysis of the ketones by Norrish I and Norrish II reactions produces various species that give rise to carboxylic acids or lactones, and to vinyl unsaturated groups (from Norrish II reactions). The secondary hydroperoxides produced by oxidation of the PE sequences can directly decompose by a mechanism that involves a radical attack and hydrogen abstraction followed by a β-scission [29]. It has also been noted that direct absorption of the shortest wavelengths by the acetate groups is likely to undergo a Norrish type II reaction that produces vinylenes and acetic acid.

Table 3
Attribution of infrared absorption bands of EVA film (identification based on analysis of the literature data [27]

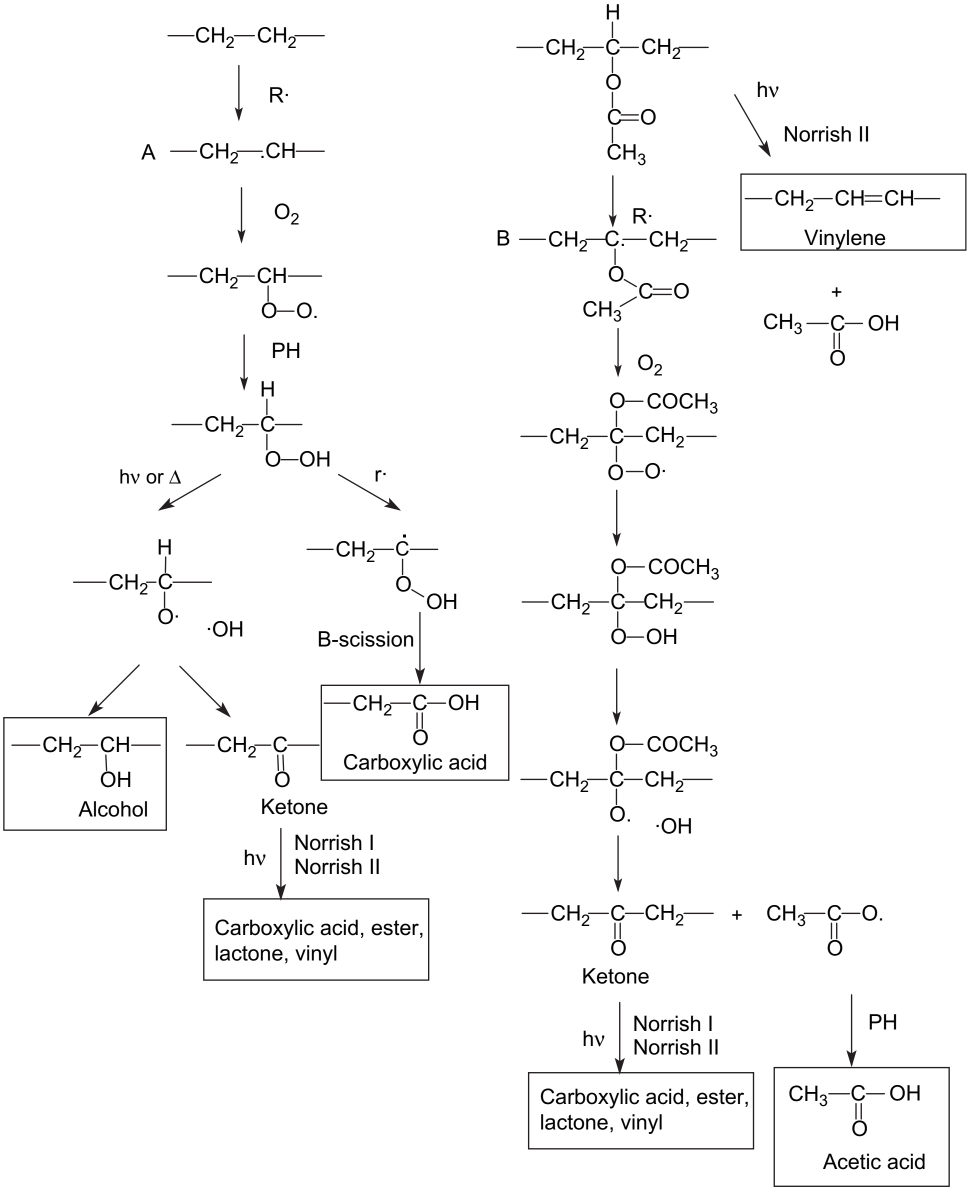
ν (cm^{-1})	Attribution
1740	ν(C=O)
1465	$\delta(CH_3)$as
1370	$\delta(CH_3)$s
1245	ν(C–O–C)s
1025	ν(C–O–C)as
720	$\delta(CH_2)$ “rocking”

3.2. Photooxidation of EVA nanocomposites made with purified MWNTs: influence of the relative amount of NTs

3.2.1. Infrared analysis

The IR spectrum of EVA/MWNTs nanocomposite with 1, 3 or 5% MWNTs before irradiation (Fig. 2a) shows only the expected absorption bands of the EVA polymer matrix, no characteristic absorption bands due to NTs have been detected. The presence of NTs gives a black colour to the nanocomposite films that leads to a shift and a slope of the baseline.

In the carbonyl domain, the general evolution of the IR spectra of EVA/MWNTs nanocomposite films under irradiation in presence of oxygen (Fig. 2a) is similar to that of a virgin EVA film. The broadening of the acetate band at 1740 cm^{-1} can be noticed (Fig. 2b). The subtracted spectra reveal the formation of carboxylic acid and lactone, respectively, at 1718 and 1780 cm^{-1}, with the same relative intensities. In the domain of the hydroxyl and unsaturated functionalities the situation is by far different. Depending on the amount of MWNTs, an influence of the NTs can be noted. One can observe the formation of the same absorption bands as reported above in the case of pristine EVA (3520, 909, 960, 990 cm^{-1}), but the intensities of these absorption bands are considerably lowered when the amount of MWNTs increases. This is illustrated by Fig. 3, which compares the evolution of the



Scheme 1. Mechanism of photooxidation of EVA (from Refs. [26,29]).

concentrations of vinyl unsaturation of the different samples to the absorbance at 1718 cm^{-1}. The formation of alcohols and unsaturation during photooxidation is dramatically reduced in the presence of MWNTs. A plateau is reached for a concentration of 3%.

3.2.2. Rates of oxidation

The rates of photooxidation of EVA in the various samples can be compared by measuring the increase of absorbance at 1718 cm^{-1} (as measured on the subtracted IR spectra) with the irradiation time (Fig. 4).

Fig. 4 shows the variations of absorbance at 1718 cm^{-1} as a function of irradiation time for the EVA/MWNTs nanocomposite films with increasing percentages of carbon nanotubes. Noteworthy is the fact that the rates of photooxidation are similar for the samples with 1% of MWNTs and for the EVA, which indicates that 1% of MWNTs has no stabilizing effect. The nanocomposite with 3% of MWNTs displays a lower rate of photooxidation. However, this stabilizing effect does not increase significantly with the concentration of MWNTs and the kinetic curves for the samples with 3 and 5% of MWNTs are very close.

3.2.3. Discussion

For the sake of comparison, it is worth first discussing carbon black as "conventional" additives in polymers. Indeed, carbon black is another carbon-based filler used for years in filled polymers. Carbon black has a dual effect on the photooxidative behaviour of polymers. On one hand, carbon black protects the polymer from photooxidation by decreasing the light intensity that is absorbed: carbon black acts as an inner filter, which results in a decrease of the rate at which the

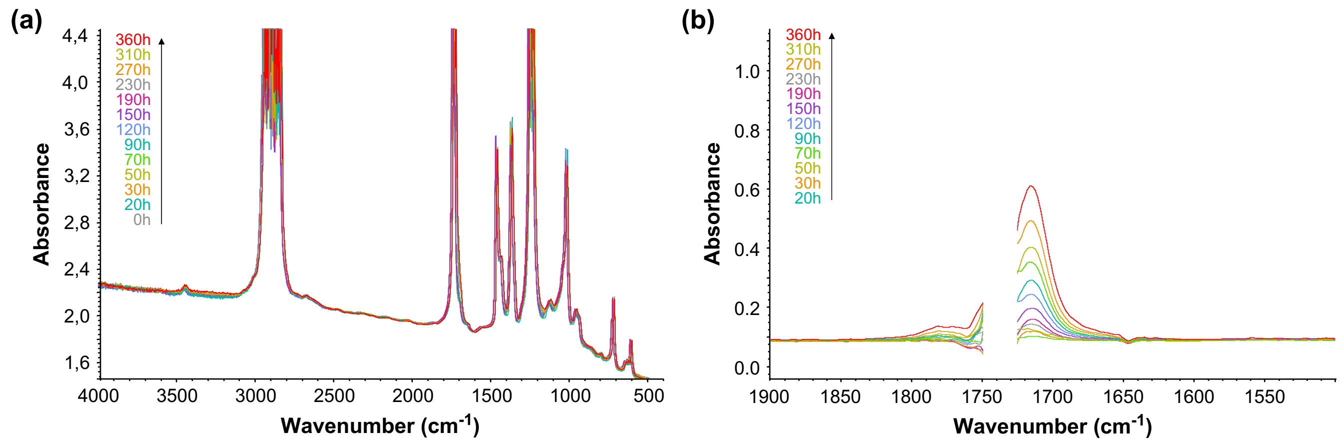


Fig. 2. FTIR spectra of a EVA/MWNTs (3%) film photooxidised at $\lambda > 300$ nm, 60 °C; (a) direct spectra in the domain 4000–400 cm^{-1}; (b) subtracted spectra (Ft − F0) in the domain 1900–1500 cm^{-1}.

polymer is oxidized by a photochemically induced process. Carbon black is also known to play a role of antioxidant [30], via catalytic decomposition of peroxides and free radical scavenging, which gives a stabilizing effect in terms of photooxidation. On the other hand, at weak concentration of carbon black, the absorption of light by carbon black is likely to provoke an increase of the local temperature by dissipation of the photon energy into thermal [31]. This can result in an increase of the oxidation rate by a thermally induced process. Competition between these two antagonistic effects (anti- and pro-oxidant) depends on several factors, including the percentage and the type of carbon black, and also the particle size, the dispersion and the structure of the polymer [32]. The influence of carbon black on the photodegradation of polyolefins such as polypropylene has been studied [32]. The results show that the presence of carbon black nanoparticles (diameter of about 20–60 nm) significantly increases UV durability of the filled polymer, especially with small particle sizes. The physical nature of carbon black accounts for its stabilizing activity and is associated with its UV absorption ability. Carbon black is reported to act as a powerful UV absorber [30], decreasing the particle size and increasing the specific surface area (both closely related) of the carbon black results in greater stability. It also contributes to a higher absorption and back scattering of the light.

Former results concerning the influence of carbon black on the photooxidation of PE [31] have shown that at low amounts, carbon black is likely to induce photodegradation. A stabilizing effect was only observed for percentages of carbon black higher than 5%. The incident light that is absorbed by carbon black is converted into thermal energy. At low concentrations of carbon black (less than 1% w/w), the thermal energy is located on the absorbing sites and the local temperature increases. This is likely to produce thermal oxidation of the polymer, or at least to dramatically increase the rate of the photothermal oxidation (it is recalled that the activation energy

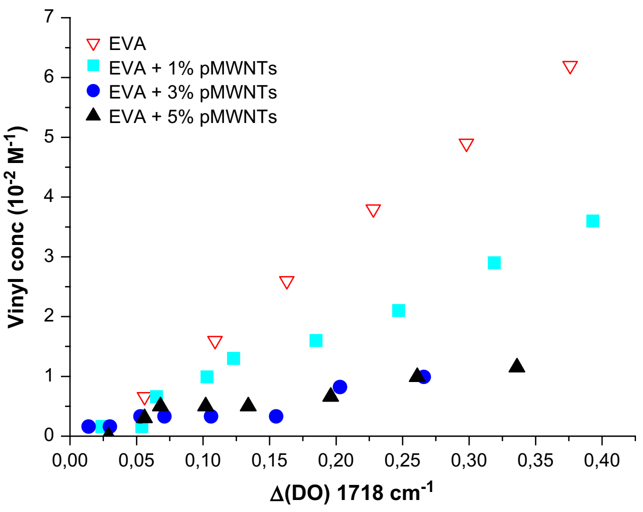


Fig. 3. Evolutions of the vinyl concentrations (measured from the absorbance at 909 cm^{-1} considering $\varepsilon = 122 \pm 7\ M^{-1}\ cm^{-1}$) versus absorbance at 1718 cm^{-1}.

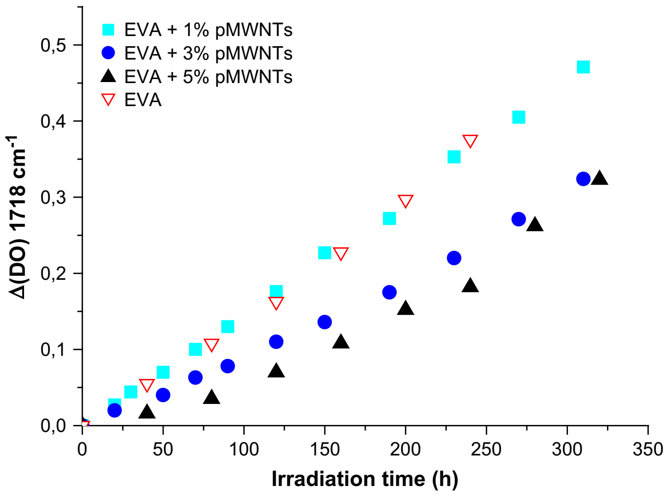


Fig. 4. Variations of absorbance at 1718 cm^{-1} as a function of irradiation time (photooxidation at $\lambda > 300$ nm, 60 °C) for nanocomposite films with 1, 3, 5% of MWNTs and an EVA film.

for the photooxidation of polymers is quite important). At higher concentrations of carbon black, the same phenomena occur, but the dissipation of the thermal energy by conduction in the material prevents from an increase of the temperature, which makes the thermal oxidation or the acceleration of the photothermal oxidation less important.

Interestingly enough, the results reported in this article in the case of MWNTs can be explained by analogy to carbon black. Initially, two effects (filter effect and thermal effect) have to be considered in order to explain the influence of the amount of MWNTs on the rates of oxidation of the EVA matrix. In the case of the samples with 1% MWNTs, practically no stabilizing effect is observed. This indicates that the filter effect of MWNTs is antagonised by the increase of the local temperature and the consequence is an increase of the rate of oxidation. Increasing the amount of MWNTs increases the filter effect and enhances the dissipation of the thermal energy. This results in a notable gain in photostability of the polymer. Noteworthy is the fact that the mechanism of photooxidation of the EVA matrix is slightly different in the presence of MWNTs. Interestingly, the decrease of the rate of oxidation (measured by the formation of the carboxylic acids) is accompanied by a much lower concentration of unsaturation and alcohols. It is indeed recalled (Scheme 1) that the formation of the hydroxyl functionalities detected by infrared analysis of the photooxidised EVA involves the photolysis of the hydroperoxides. In parallel the vinyl unsaturation is formed by Norrish photolysis of the ketones. The presence of MWNTs at the highest concentrations used here (3 and 5%) is likely to protect both these photochemically unstable products by a screen effect. Similar conclusions can be drawn concerning the weak concentrations of vinylene groups, formed by Norrish II reaction of the acetate groups, which reflects the screen effect of MWNTs.

A third effect has to be considered: the potentiality of MWNTs in acting as antioxidants. Results published by Billingham et al. [33] have shown that carbon nanotubes can act as weak antioxidants stabilizing the polymer upon heating. It is then very probable that the antioxidant effect of MWNTs participates in stabilizing the EVA matrix. It is, however, difficult to discriminate between the three effects, inner filter, antioxidant and at the same time oxidation inducer as a result of higher local temperatures. One can only consider the whole effect that is observed.

3.3. Influence of the morphology

Analogy with the behaviour of carbon black permits anticipating that the photochemical activity of carbon nanotubes is closely linked with their structure, morphology and surface treatment. For this reason, investigations of the photochemical behaviour of a series of EVA with different types of NTs were carried out.

3.3.1. Influence of the MWNTs morphology (3 wt% of MWNTs)

Fig. 5 compares the time-dependent evolution of the carboxylic acids (absorbance at 1718 cm^{-1}) for nanocomposite films with 3 wt% of crushed, thin and purified MWNTs that have different morphologies as described above in Table 1. First of all, it is worthy to note that the concentrations of hydroxylated and unsaturated photoproducts that develop are similar for the three types of samples, purified, crushed and thin MWNTs.

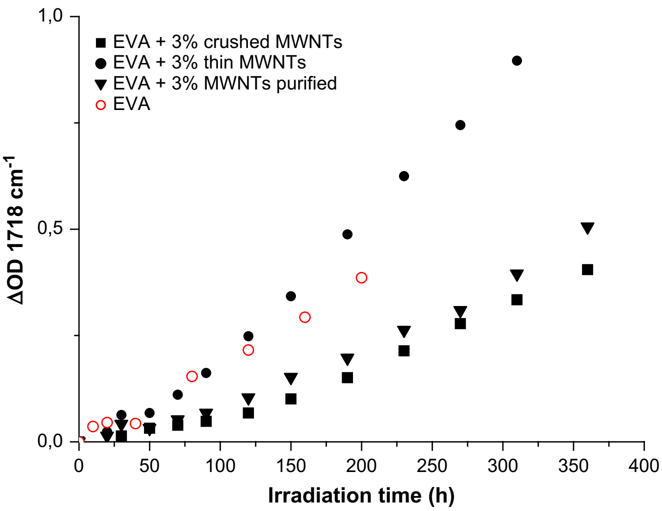


Fig. 5. Variations of absorbance at 1718 cm^{-1} as a function of irradiation time (photooxidation at $\lambda > 300$ nm, 60 °C) for nanocomposite films with 3% of NTs depending on the type of MWNTs.

Marked differences exist between the kinetics of photooxidation. The kinetic curves presented in Fig. 5 reveal a marked influence of the morphology of multi-walled carbon nanotubes on the oxidation rates. Crushed MWNTs have a stabilizing effect that is similar to the effect of purified MWNTs. Surprisingly, in the case of nanocomposite film filled with thin MWNTs, a notably higher oxidation rate is noted, which is even more important than in the case of the EVA reference sample.

Morphological characterization by TEM and AFM [8] showed a rather limited extent of NTs dispersion in EVA, many agglomerations were still visible forming long bundles of NTs. The crushed MWNTs have a much shorter length and intermediate flexibility that provide a better nanotube dispersion. There is more likely an effect of the aspect ratio of this kind of nanotubes with much reduced length. Longer carbon nanotubes, e.g. purified MWNTs, might trigger a higher degree of interconnectivity that leads to a significant reduction of the nanofiller dispersion and poor mechanical properties [8]. However, this does not seem to have an influence on the EVA oxidation.

In the case of thin MWNTs, the different parameter is the diameter of the filler. The stabilizing effect is completely lost with thin MWNTs resulting in a faster degradation of the nanocomposite (Fig. 5). The inner filter effect of MWNTs depends only on the concentration and one can assume that it is similar for the three types of MWNTs since the same amounts are used. The two parameters that have to be taken into account are the dissipation of the thermal energy and the antioxidant effect of the MWNTs. The results given in

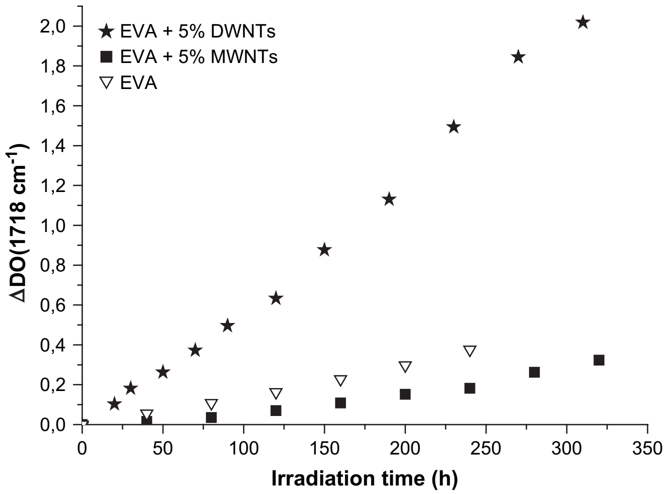


Fig. 6. Variations of absorbance at 1718 cm^{-1} as a function of irradiation time (photooxidation at $\lambda > 300$ nm, 60 °C) for nanocomposite films with 5% of MWNTs or DWNTs and for an EVA film.

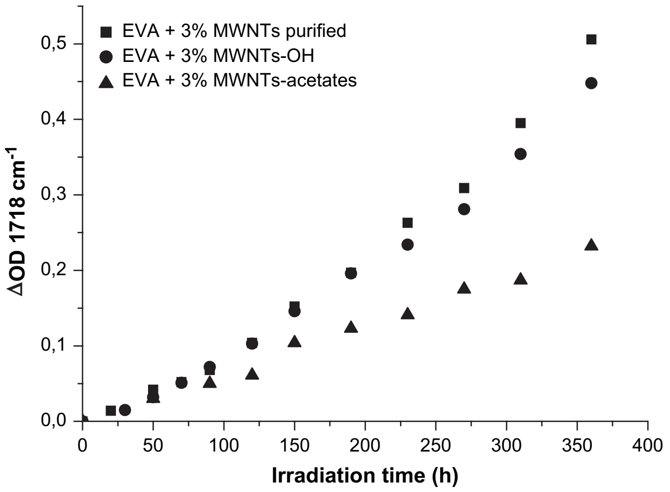


Fig. 7. Variations of absorbance at 1718 cm^{-1} as a function of irradiation time (photooxidation at $\lambda > 300$ nm, 60 °C) for nanocomposite films with 3% of functionalized MWNTs.

Fig. 5 could be explained on the basis of an increase of the local temperature resulting from the light absorption and a weak dissipation of the thermal energy. As recalled above, this could cause in turn an increase of the photooxidation rate and also participate in the thermal oxidation of the polymeric matrix. The second effect that has to be considered is a decrease of the antioxidant activity of the MWNTs as a result of its different geometry.

3.3.2. Influence of the type of NTs (5 wt% of NTs)

A last series of experiments were carried out in order to characterize the influence of the type of NTs (multi-walled versus double-walled). As reported above in the case of the samples with 5% of purified MWNTs, the relative concentration of unsaturated and hydroxyl functionalities was dramatically reduced (for a similar extent of oxidation measured by the concentration of carboxylic acids), which confirms the inner filter of the purified MWNTs.

Fig. 6 shows the rate of photooxidation of the sample made with the double-walled carbon nanotubes (DWNTs). The behaviours of both the pristine EVA and the sample made with the purified MWNTs are also shown in this figure.

It is clearly observed that the EVA/DWNTs nanocomposite degrades much faster than pristine EVA and EVA/MWNTs. The stabilizing effect is completely lost. These DWNTs dramatically induce the photodegradation of EVA. DWNTs are carbon nanotubes with lower dimensions, both in diameter and length. On the basis of the results commented above about the influence of the nanotube morphology (Fig. 5), it is very probable that this inducing effect of DWNTs comes from the different geometry of these nanotubes, which could modify their ability in dissipating the thermal energy and could also drastically influence their antioxidant activity.

3.3.3. Influence of the surface-modification of NTs

The influence of the functionalization of carbon nanotubes was also studied, by comparing the rates of photooxidation of samples made with 3% of purified MWNTs or MWNTs functionalized either with hydroxyl groups (MWNTs-OH) or with acetate groups (MWNTs-Ac). The kinetic curves given in Fig. 7 show that very similar stabilizing effects are obtained with MWNTs and MWNTs-OH. This result indicates that the presence of OH groups does not modify the degradation of the EVA matrix. In the case of the functionalization with acetate groups, a notable decrease of the oxidation rate was observed, which makes this sample the most stable in the series already investigated.

3.3.4. Effect of HDPE coating MWNTs

Photooxidation of films of the EVA/MWNTs-PE nanocomposites was carried out to evaluate the influence of the destruction of the bundles and as a consequence the influence of the dispersion of NTs in the EVA matrix. Fig. 8 compares the rates of photooxidation of the EVA nanocomposites with the PE-coated MWNTs and the purified MWNTs at the same concentration (3% NTs).

The EVA nanocomposites filled with MWNTs-PE display a higher degradation rate than the homologous EVA/MWNTs, and only a weak stabilizing effect is observed.

4. Conclusions

The behaviour of carbon nanotubes as antioxidants has already been reported [33] and polymer/multi-walled carbon nanotubes nanocomposites with different matrices such as PS, PP, PE were studied in order to understand how carbon nanotubes can affect the stability of polymers at elevated temperatures. The results show that MWNTs can act as weak antioxidants, stabilizing the polymers upon heating. The antioxidant effects in polymeric materials have been attributed to the strong radical accepting capacity of NTs. This activity comes from their electron affinity (similar to the C_{60} (ca. 2.65 eV)) [34], which may interrupt chain propagation. By analogy to C_{60}, NTs were predicted to behave as radical traps

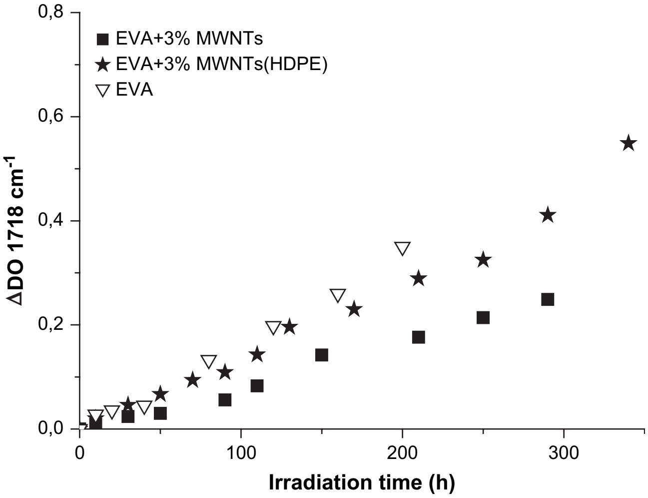


Fig. 8. Variations of absorbance at 1718 cm^{-1} as a function of irradiation time (photooxidation at $\lambda > 300$ nm, 60 °C) for nanocomposite films with 3% of MWNTs, or 3% of MWNTs-PE or without NTs.

in chain reactions. Nevertheless the effect is weak compared to phenolic antioxidants but comparable with the effect of carbon black. In conditions of photooxidation, one has to take into account the absorption of UV-light which can produce two antagonistic effects: an inner filter effect which is likely to participate in a decrease of the photochemically induced oxidation and at opposite an increase of the local temperature, which can provoke a thermo-oxidation of the polymer matrix or increase the rate of the photothermal oxidation. The antagonism between both these effects produces either a stabilizing or a prodegradant effect.

As a conclusion one has to consider that NTs play three roles: NTs can act as inner filter, as antioxidant and/or as prodegradant filler by a local increase of temperature. The competition between the two antagonistic effects, anti- and pro-oxidant depends on several factors, including not only the percentage and the type of carbon nanotubes, but also their morphology and their dispersion. The screen effect is related to the concentration of NTs, and the antioxidant effects as well as the dispersion of the nanofiller depend on the structure of the NTs.

The results given in this article show that the global effect of NTs results mainly in a stabilizing effect on the nanocomposite degradation when the amount of NTs is higher than 1% w/w. However, two kinds of the NTs studied (thin MWNTs and DWNTs) have shown a higher degradation than the pristine EVA, which reveals a lower ability to act as antioxidant and/or a modification of their ability in dissipating the thermal energy. The size effect of carbon black particles on photodegradation previously reported [32] might be enhanced with the morphology and aspect ratio of carbon nanotubes. Carbon nanotubes display a higher specific surface area than carbon black, which could explain the influence of the carbon nanotube morphology, with an effect mainly of the diameter. Long carbon nanotubes are extremely difficult to disperse in EVA, actually forming well-known associated bundles.

The simultaneous addition of organo-clay and carbon nanotubes gives a peculiar morphology: good extent of clay platelet exfoliation and partially dispersed long nanotubes with high degree of interconnectivity. This new type of nanocomposites displays a synergistic effect on the thermal and flame retardant properties [1,8]. In order to compare the influence of carbon nanotubes and clays as nanofillers, the photochemical behaviour of EVA/clay nanocomposites is currently under investigations. And the next step of this study will be the photodegradation of ternary nanocomposites based on EVA, an organo-clay and carbon nanotubes.

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