DOI: 10.1002/masy.201150303

Influence of MWNT on Polypropylene and Polyethylene Photooxidation

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Summary: Nanocomposites containing multiwall carbon nanotubes (MWNT) were prepared by melt compounding with polypropylene and polyethylene. The samples were UV-light irradiated in artificial accelerated conditions representative of solar irradiation ($\lambda > 300$ nm) at 60 °C in air. The chemical modifications resulting from photooxidation were followed by FT-IR spectroscopy. The behaviour of nanocomposites containing MWNT depends from the type of polymer and presence or absence of antioxidant. The presence of MWNT affect photooxidation of the two polymers working as an UV-screener on the other hand the increase of thermal oxidation provoked by conversion of photon energy into thermal partially balance the decrease of positive effects on oxidation rate. The negative effects can be minimized by the presence of antioxidants that show interesting synergistic effects with MWNT.

Keywords: Carbon nanotubes; nanocomposite; photooxidation; polyethylene; polypropylene

Introduction

Nanocomposites formed by inorganic nanofiller in a polymer matrix are a new class of important materials. Introduction of quantities lower than 5%wt of nanodispersed inorganic particles offers performance similar to conventional polymeric composites with 30-50%wt of reinforcing fillers. Improvements in performances such as modulus, heat resistance, dimensional stability, barrier properties and flame retardant performance are often obtained simultaneously.[1–3] Carbon nanotubes (CNT) were discovered in 1976 by Endo et al.[4] Since elucidation of the structure by Iijima in 1991,[5] CNT were widely studied for their exceptional mechanical properties[6–8] but also for their electrical[9] and thermal conductivity.[10] Moreover carbon nanotubes, as demonstrated from this group, shows interesting properties as polyolefines flame retardant additive.[11,12] Because of the increase of production capacity in the last years the cost of MWNT decreased by a factor 10-100. Actually carbon nanofibers and multi-wall carbon nanotubes (MWNT) are beginning to meet price barriers for most applications and will start seriously competing with current technologies.

The resistance to UV-light is a key factor for most outdoor applications of polymeric materials; in the case of nanocomposites based on polyolefines, practically all studies reports that nanocomposites degrade faster than pristine polymers.[13–17] In a recent article Morlat et al.[18] demonstrate a CNT anti-oxidant effect of CNT/EVA nanocomposites while Dintcheva et al.[19] show as the stabilization effect depends from MWNT concentration and presence of UV-stabilizers. More generally it should be pointed out that the CNT have a great absorption in the UV-visible light. It could be imagined that at the same way as for other filler highly light-absorber (e.g. carbon black) CNT stabilize polymers also from the photo-oxidant point of view. This paper reports on the study of the photodegradation of nanocomposites based on

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polypropylene and polyethylene as polymer matrix and on MWNT as carbon nanotubes. The chemical modifications resulting from photooxidation were investigated by infrared spectroscopy. The influence of carbon nanotubes on the mechanism of oxidation of the polypropylene (PP) and polyethylene (PE) was evaluated. The rates of degradation of PP/MWNT and PE/MWNT nanocomposites were compared with pristine polymers before and after antioxidant extraction.

Experimental Part

Materials

Polypropylene, HP500 N (PP) supplied by Basell S.p.A. was used. Linear low density polyethylene (PE) "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 Table 1.

Melt Processing

Nanocomposites containing 3%wt of MWNT were prepared via melt-blending using a Brabender Plasticorder PLE851 internal mixer at 120 °C for LLDPE, 180 °C for PP. MWNT and polymers were introduced slowly at 10 r.p.m. in order to use polymer pellets and partially melted polymer as milling agent to disaggregate MWNT bundles thus MWNT and polymers were melt-blended at 60 r.p.m. for 10 minutes. Blank samples were prepared by processing LLDPE and PP without MWNT. Film specimens for photooxidation were prepared using a hydraulic press with the two heated plates at 190 °C using a pressure of 25 Bar for 1 minute.

Table 1.
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

Extraction

Extractions to eliminate antioxidant were carried out using a solution n-hexane/ethanol/chloroform 4/1/1 in weight for 24h at 60 °C. Extractions were continued until UV evidence of antioxidant presence disappeared.

Irradiation

Irradiations of nanocomposite films were carried out in air in a SEPAP 12/24 unit (ATLAS) at $\lambda > 300$ nm and 60 °C. This apparatus is equipped with four medium-pressure mercury lamps with borosilicate envelope which filters wavelengths below 300 nm and it is designed for the study of accelerated artificial photodegradation, in conditions that are relevant to natural outdoor weathering.[20]

Characterization

Infrared Spectra of films were recorded with a using a Perkin-Elmer Spectrum GX Infrared Spectrometer. Spectra were obtained using 32 scans and a 4 cm^{-1} resolution.

PP photooxidation was followed by the intensity 1712 cm^{-1} peak which was plotted as a function of time, in order to avoid differences due to film thickness absorption was normalized to the IR absorption band at 2723 cm^{-1} ($\upsilon_{(C\text{-}H)}$ vibration stretching band of PP). PE photooxidation was followed using the area of carbonyl band (area between 1850-1600 cm^{-1} maximum at 1715 cm^{-1}) normalised by the area of the rocking vibration bands of CH_2 (area between 969 and 757 cm^{-1}).

Because of the high absorbance typical of samples containing MWNT, it was necessary to check the linearity of these normalization methods, thus a commercial sample of PP containing grafted maleic anhydride was mixed with 3%wt of MWNT using the same condition of prepared nanocomposites. The 1781 cm^{-1} band, typical of cyclic anhydride, was normalised for both samples using the 2723 cm^{-1} band, this experiment evidenced as the confidence for this method was about 95% that is in line with tolerance between different samples of the same study.

SEM Analyses were performed with a LEO 1450 VP using the backscattered modality on surface of fragile fracture from film samples fractured after cooling by immersion in liquid nitrogen. The samples were metalized with gold.

Result and Discussion

SEM Characterizations

The SEM characterization of PPMWNT (Figure 1) evidenced as it was possible to obtain a good dispersion of MWNT only by optimization of melt-blending process, PPMWNT show the presence of only small aggregated (yellow arrows Figure 1a) composed of few MWNT. From SEM characterization MWNT results dispersed in PE even better than in PP (Figure 1c,d).

Photooxidation of Nanocomposites

The infrared analyses of the polypropylene and MWNT nanocomposites show only the expected absorption band of polypropylene: MWNT have no characteristic bands in the infrared as already described elsewhere.[21]

The photooxidation mechanism of isotactic PP has been reported numerous times in the literature.[18,22,23] The main product of the combined action of UV-radiation and oxygen is the formation of the tertiary hydroperoxide. The oxidation continues up to the production of carboxylic acids, esters, peresters lactones and other oxidised species.

The infrared analysis of PP photooxidation shows the formation of a band with a maximum at 1712 cm^{-1}(Figure 2). These modifications indicate the formation of carbonylic band from the oxidated species. In the hydroxyl region, a broad absorption band is observed with a maximum at 3400 cm^{-1} that corresponds to products

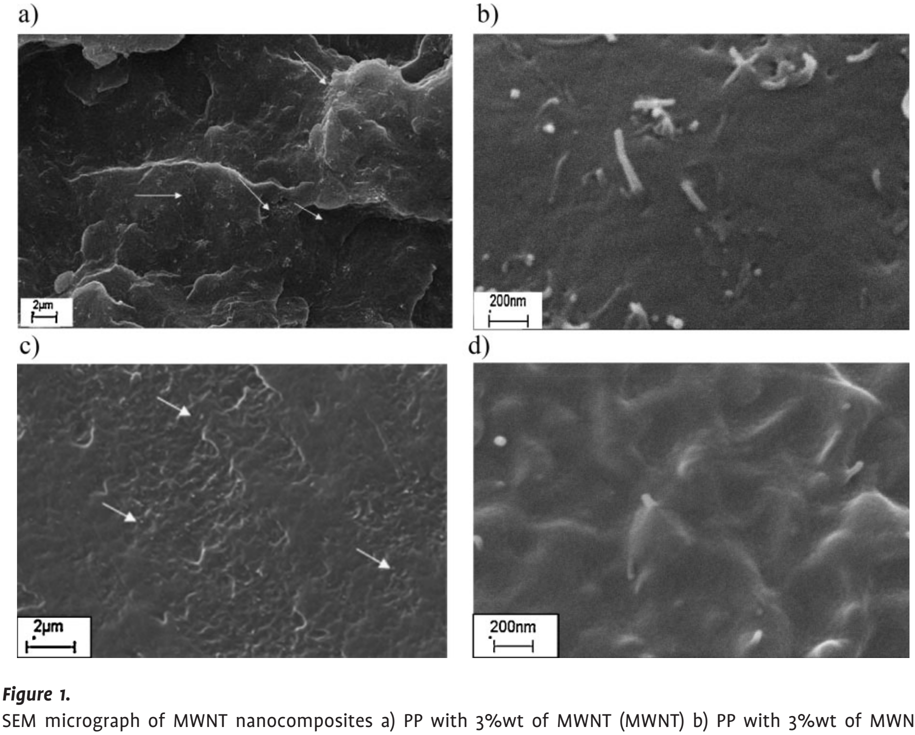

Figure 1.

SEM micrograph of MWNT nanocomposites a) PP with 3%wt of MWNT (MWNT) b) PP with 3%wt of MWNT c) d) LLDPE with 3%wt of MWNT.

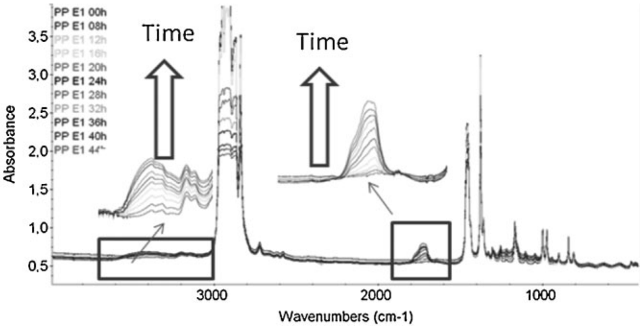

Figure 2.
FTIR spectra of a PP film versus photooxidation time at $\lambda > 300$ nm.

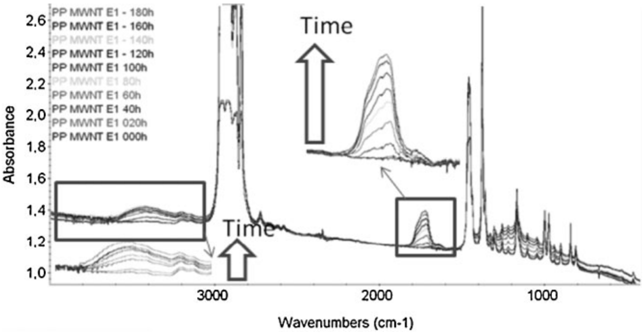

Figure 3.
FTIR spectra of a PPMWNT film versus photooxidation time at $\lambda > 300$ nm.

such as hydroperoxides and alcohols. The infrared analyses of PPMWNT photooxidation show the formation of bands similar to what already found for PP. Thus in this case the MWNT presence do not change the photooxidation mechanism.

The oxidation induction time increases for PPMWNT for samples before and after extraction (Table 2) on the contrary the oxidation rate decreases (Table 2, Figure 4a-b). It can be supposed that MWNT works as an inner filter decreasing the percentage of radiation available for photooxidation and thus the oxidation rate. Probably this effect is partly compensated by the increase of oxidation rate provoked by thermal oxidation due to dissipation of the photon energy into thermal. On the

Table 2.
Oxidation induction time (OIT) of PP and PE pure polymer and MWNT nanocomposites. rate of oxidation (rate) obtained from normalised absorption at 1712 cm^{-1} of PP and PP/MWNT nanocomposites before and after extraction.

Sample	Before extraction		After extraction	
	OIT (h)	Rate (a.u.)	OIT (h)	Rate (a.u.)
PP	8	0.056	4	0.080
PPMWNT	28	0.022	20	0.028
PE	20	–	12	–
PEMWNT	100	–	36	–

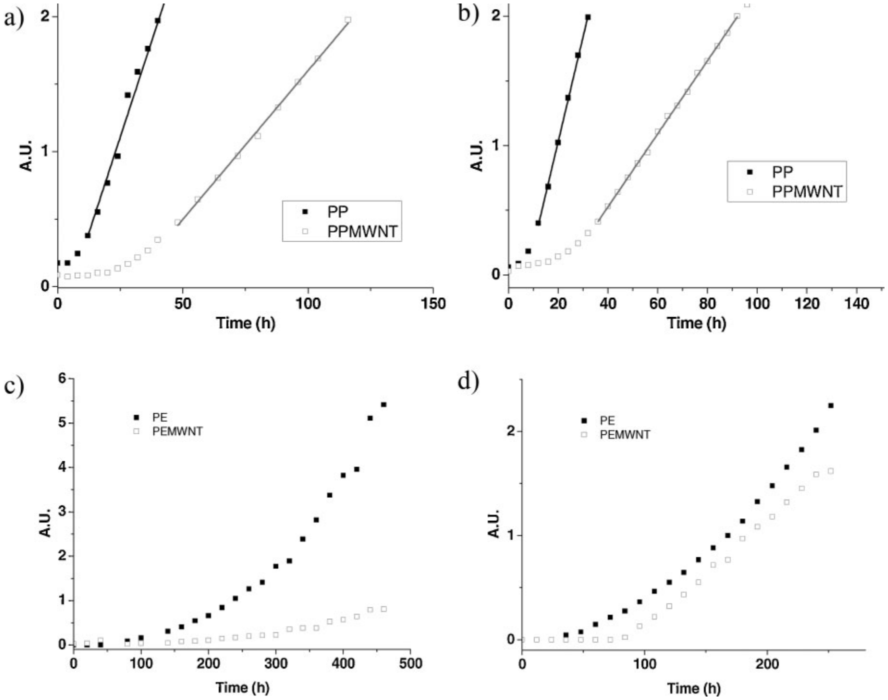

Figure 4.
photooxidation at $\lambda > 300$ nm, 60 °C of film of PP, PPMWNT (normalised absorption at 1712 cm^{-1} versus time) and PE and PEMWNT (normalised absorption of carbonyl band) a) PP and PPMWNT before extraction b) PP and PPMWNT after extraction c) PE and PEMWNT before extraction d) PE and PEMWNT after extraction.

basis of the modest increase of OIT in the case of polypropylene MWNT does not work as antioxidant.

Photooxidation of PE is known to result in the formation of hydroxyl and carbonyl groups. The nature of the main oxidation products is well-established and the mechanisms by which oxidation occurs can be considered as fairly well understood.[24,25] Modifications of the IR spectra indicate the formation of ketones and acids at 1715 cm^{-1}, esters at 1730 cm^{-1}, γ-lactones at 1780 cm^{-1}, hydroperoxides and alcohols at 3420 cm^{-1} and unsaturation at 910, 965 and 990 and 1640 cm^{-1}. The carboxylic groups are mainly formed by the hydroperoxyde decomposition thermally- or photo- activated while the unsaturation are formed mainly by Norrish reactions (Figure 5), thus a typical photoreaction.

In Figure 6 the 1640 cm^{-1} band of unsaturation formed during PE photooxidation is evidenced.

The modifications of the IR spectra of film of LLDPE/MWNT resulting from photooxidation are shown in Figure 7. The observed modifications of the spectrum are quite similar to those of pristine LLDPE. In the carbonyl domain, it can be observed that the absorption bands that

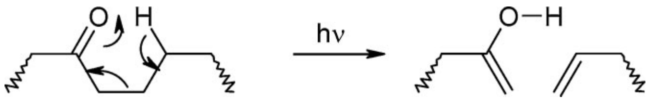

Figure 5.
Norrish II reaction.

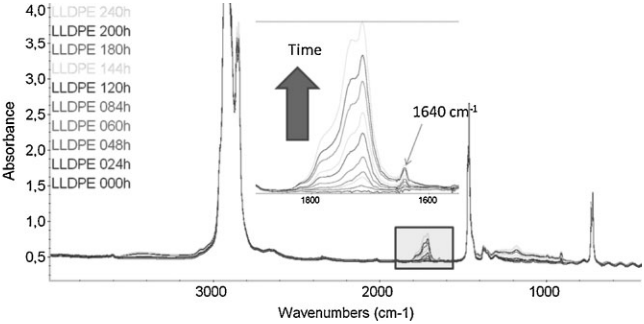

Figure 6.
FTIR spectra of a PE film versus photooxidation time.

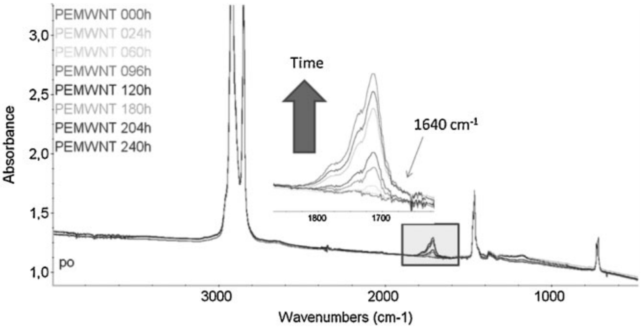

Figure 7.
FTIR spectra of a PEMWNT film versus photooxidation time.

develop under irradiation are similar to those of a virgin PE film however in this case there is no trace of 1640 cm^{-1} band due to unsaturation.

During photooxidation the concentrations of ketones and vinyl groups increase linearly with the time of exposure whereas carboxylic acids accumulate exponentially.[26] The absence of unsaturations means that MWNT work as an UV-screener and oxidation of PE is in mainly part not due to photooxidation. On the other hand the absorption of light by MWNT is likely to provoke an increase of temperature by dissipation of the photon energy into thermal. This can result in an increase of the oxidation rate by a thermally induced process without formation of unsaturations.

On the basis of these considerations the presence of process antioxidant seems to work in synergy with MWNT increasing the oxidation induction time of PEMWNT not extracted of about 80 h on the contrary of what happen for extracted samples where the difference of OIT is only of 24 h (Table 2). The oxidation rate evaluated on the basis on growth of carbonyl band absorbance (Figure 4c-d) shows similar results, in presence of process antioxidant the oxidation rate is lower for PEMWNT while, after extraction the oxidation rates are quite similar. Thus the increase of thermal oxidation in PEMWNT practically compensate the UV filter effect of MWNT.

Conclusion

Polypropylene and polyethylene MWNT based nanocomposites were exposed to photooxidation. In this case the MWNT work as UV absorber decreasing the photooxidation rate of both polymers. On the other hand the absorption of light by MWNT is likely to provoke an increase of temperature by dissipation of the photon energy into thermal provoking an increase of thermal oxidation. In the case of polypropylene the overall effect is positive with the decrease of oxidation rate. In the case of polyethylene in presence of MWNT the positive effects are practically balanced by the negative effects thus the presence of an antioxidant is necessary to obtain a decrease of oxidation rate by a synergistic effect.

Acknowledgements: We thank Prof. Giovanni Camino (Politecnico di Torino sede di Alessandria) for the feedback and comments.

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