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THERMAL AND SPECTROSCOPIC CHARACTERIZATION OF POLYPROPYLENE-CARBON NANOTUBE COMPOSITES

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Thermogravimetric (TG) and varied temperature Raman spectroscopic measurements of melt-blended polypropylene composites (PP) with double wall (DWNT) and multi-wall carbon nanotubes (MWNT) revealed that the incorporation of carbon nanotubes into polymer matrix increased the thermal stability comparing to the virgin polypropylene. The characterization of reference nanotubes was also done by Raman microscopy and TG measurements. Varied temperature rheological analysis provided further information about the thermal decomposition of the composites indicating the formation of high strength char in case of MWNT and limited applicability of DWNT at high temperature. The residue of the decomposition of PP-MWNT nanocomposites consists of nanotubes of spectroscopically higher purity comparing to the original one indicating the thermally induced chemical changes in the solid phase.

Keywords: *DWNT, MWNT, PP composites, TG*

Introduction

Introduction of nanoscale particles into polymer matrices often leads to considerably enhanced physical properties. Nanotubes may influence the crystallization and melting behaviour of polymers [1]. Furthermore the increasing application of nanofillers in the field of polymer composites makes clear their mostly positive influence on the thermal stability of polymers. The thermal stability in turn is in close connection with the fire retardancy [2].

A large variety of polymers have been used as matrix in the preparation of carbon nanotubes/polymer nanocomposites [3]. Polypropylene (PP) is one of the most commonly used one, owing to an attractive combination of benefits like low cost, low mass, good balance of properties, processability and wide field of application. The carbon nanotubes (CNT) show electrical properties as well as high thermal conductivity properties in the axial direction [4], thermal conductivity being ca. 1750–5800 W mK^{-1} [5].

The thermal properties of CNTs/polymer composites attracted many attentions from polymer scientists because of the relatively high thermal stability of CNTs [6]. Moreover, polymer nanocomposites containing low percentages of carbon nanotubes have been reported recently to possess significantly increased thermal stability together with electrical and thermal conductivity properties [7].

The aim of this work is to evaluate the effect of DWNT and MWNT on the thermal degradation of polypropylene based nanocomposites prepared in a batch mixer at various content and types of nanotubes. The effect of different atmospheres i.e. air (as oxidative) and nitrogen (as inert) were also investigated on the thermal stability of PP/nanotube systems. Information about the combined effect of thermal and shear stress on the samples was intended to gain by means of thermal scanning rheometry.

Experimental

Materials

Polypropylene (PP) produced by Basell Polyolefins (Italy) was used as polymer matrix (product name: Moplen HP400R with melt flow index 25 g/10 min (230°C; 2.16 kg)). Two types of carbon nanotubes (CNT) supplied by Nanocyl (Belgium) were used: multi-wall carbon nanotube (MWNT, 95% high-purity grade) and double-wall carbon nanotube (DWNT, 90% purity) produced via CCVD process. Composites were prepared in a Brabender internal mixer W50E at 180°C, 60 rpm. Nanotubes were loaded into PP at 1 and 3 mass% [8].

Preparation of polypropylene composites

The carbon nanotubes containing PP composites were prepared using Brabender internal mixer operating at 180°C and 60 rpm for 10 min. Table 1 shows composition and the code of compounds investigated.

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Table 1 PP based CNT nanocomposites

Matrix	Filler	Filler/ mass%	Label
PP HP400R	–	–	PP
PP HP400R	MWNT	1	PP+1% MWNT
PP HP400R	MWNT	3	PP+3% MWNT
PP HP400R	DWNT	1	PP+1% DWNT
PP HP400R	DWNT	3	PP+3% DWNT

Methods

Thermogravimetry

Thermogravimetry (TG) was performed on a TA Q 500 instrument, on ca. 10 mg samples, in platinum pans, with gas fluxes of 60 mL min^{-1} for sample gas (nitrogen or air), and 40 mL min^{-1} for balance protection gas (nitrogen) on heating at 20°C min^{-1}, between 50 and 800°C. $T_{5\%}$ is defined as the temperature at 5% of mass loss and $T_{\max}$ is the maximum mass loss rate temperature (i.e. derivative TG, peak temperature).

Rheology

Varied temperature rheology measurements were carried out using an AR 2000 Thermal Scanning Rheometer (TA Instruments) in a parallel plate configuration. The thermal scanning experiments have been carried out in oscillation mode of 5 Hz while the samples were heated from ambient temperature up to 550°C with heating rate 20°C min^{-1} with normal force control, strain of 0.1%.

Raman micro-spectroscopy

Raman analyses were performed by a LabRam type confocal Raman microscope (Jobin Yvon, France). The used magnification was 100× and the excitation source was frequency doubled Nd-YAG laser emitting at 532 nm.

The thermal scanning analyses monitored by Raman microscope have been carried out on a hot-stage. The heating rate was 10°C min^{-1} and the Raman spectra were collected at every 50°C. Before the Raman measurement the sample was held at constant temperature for 5 min.

For comparison, analyses were also performed on pure PP treated in a Brabender mixer in the same condition used to prepare the composites.

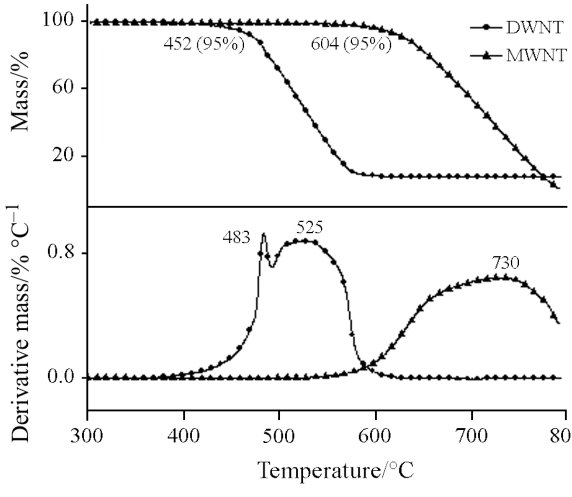

Fig. 1 TG and DTG curves in air of MWNT and DWNT

Results and discussion

Thermal stability of nanotubes

Carbon nanotubes are stable under inert conditions, the mass loss in nitrogen (not shown here) being negligible for DWNT and MWNT until 550°C.

The TG and DTG of pure carbon nanotubes in air are shown in Fig. 1. DWNT start to lose mass at ca. 450°C: a first decomposition peak, centred at 483°C, could be attributed to the more damaged tubes while the majority of the material degrades with a single large peak centred at 525°C. The degradation is complete at 600°C, leaving a 8% residue probably due to catalyst and support from synthesis. As far as MWNT are concerned the low temperature degradation peak is no more recognised: the mass loss starts at 604°C and $T_{\max}$ is found at 730°C. At the end of the analysis the degradation process is not complete. This difference can be attributed to the higher defectiveness of DWNT due to the synthetic process that makes them more subject to the degradative action of air with respect to MWNT.

The Raman spectra of CNT-s collected during increasing the temperature were comparable, the (Fig. 2a) indicate the changes of DWNT that take place through the heating of sample.

Changes in the intensities of RBM (radial breathing mode) range of samples after heating up to 450°C and recooling both of the samples have been shown that some of the changes are irreversible, the sample goes through a moderate degradation procedure. This partial degradation can be observed in optical images as well (Fig. 2b).

Figure 3 shows how the increase of intensity of the transported energy (TE) (which is directly proportional to the temperature of sample) decreases the D band, indicating that the disordered (probably mainly amorphous) part of the sample is getting oxidized. Thus the decomposition of the amorphous part is responsible for the irreversible changes seen in Fig. 2.

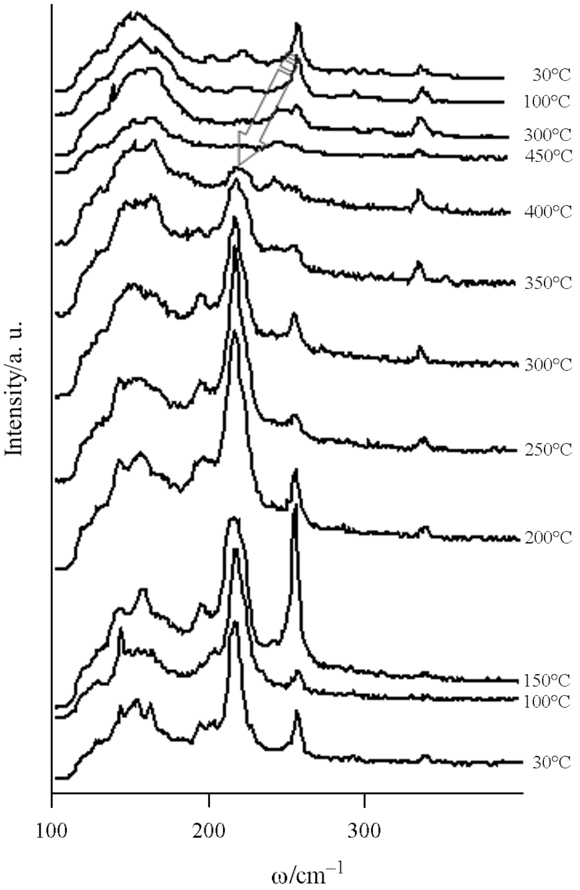

Fig. 2a Temperature dependent changes in the Raman spectra of DWNT at RBM region

Thermal stability of PP-CNT composites

TG analyses of PP-CNT composites were carried out both in nitrogen and in air atmosphere in order to get a complete picture on their thermal behavior. The results are given in Figs 4 and 5 respectively, where the curves of pure polymer matrix and CNT-containing composites are compared.

From Fig. 4, it is clear that, as already reported from some of the authors in other experimental conditions [5], pristine nanotubes in nitrogen increase both $T_{5\%}$ and T_{max} with maximum increase of 32°C for $T_{5\%}$ and of 18°C for T_{max}.

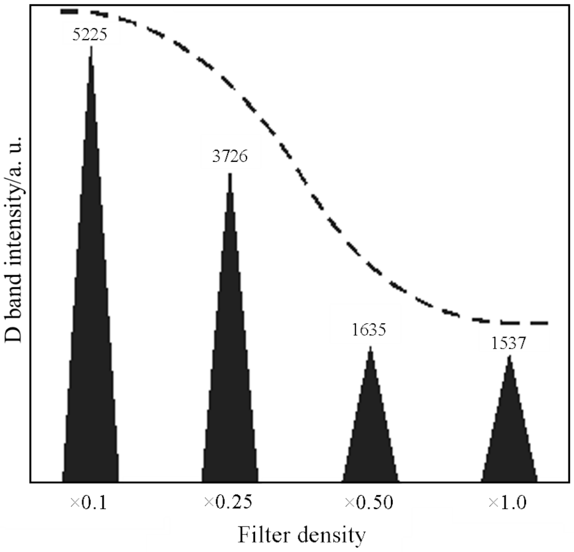

Fig. 3 The changes of intensities of D band in Raman spectra of MWNT samples at different transferred energy. (The TE was adjusted by using neutral density filters and controlled treatment time)

In air the difference between range of temperature for composites mass loss, as compared to PP, is much higher than in nitrogen and increases with CNT concentration (maximum ΔT_{max}=18°C in nitrogen and 101°C in air). A larger effect is observed for MWNT as compared to DWNT the delay in T_{max} induced by a 3% loading of DWNT is in fact very similar to that induced by a 1% loading of MWNT.

The protection action of nanotubes can be attributed to a barrier effect implying a hindered transport of polymer degradation products from the condensed to the gas phase.

The shape of the mass loss curve of PP is strongly modified by the CNT in the presence of air becoming strongly asymmetrical. If we take into consideration the 3% MWNT loaded sample, the beginning of the degradation can be fixed at 320°C, as in the case of the other samples, and the mass loss proceeds slowly up to 454°C. When this temperature is reached an abrupt acceleration of the mass loss is observed.

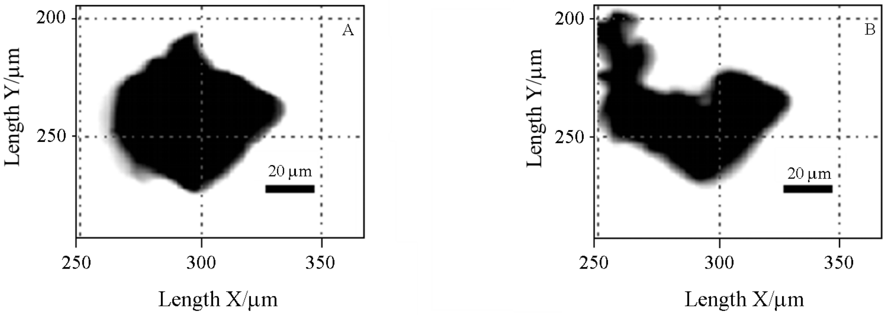

Fig. 2b The optical images of nanotube sample (DWNT) A – before and B – after Raman analysis

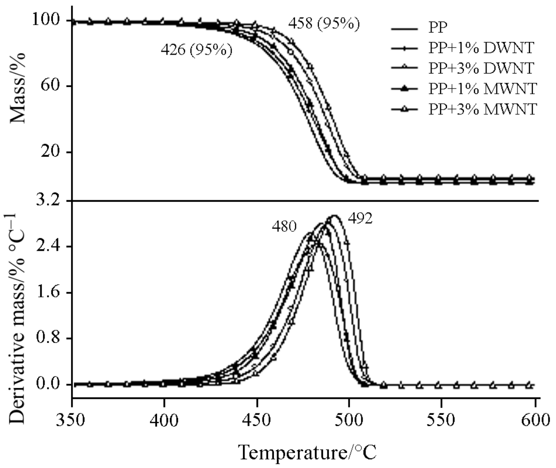

Fig. 4 TG and DTG results of PP-MWNT and PP-DWNT composites in nitrogen

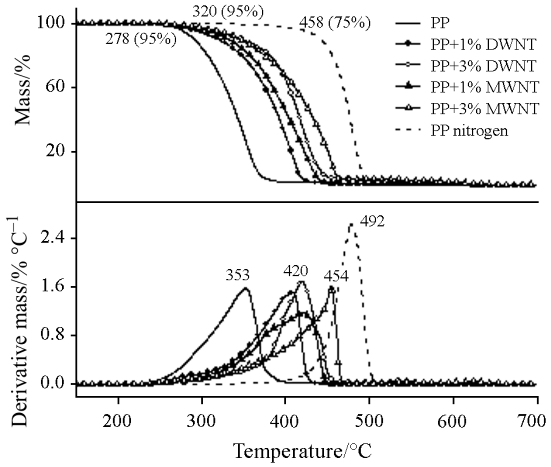

Fig. 5 TG and DTG results of PP-MWNT and PP-DWNT composites in air

As already stated in a previous paper [5], such behaviour can be attributed to the formation of a superficial protecting nanotube network which is destroyed when increasing the temperature up to a limit value. The protection from oxygen action is therefore extremely efficient at low temperatures but the final result is in any case a complete degradation of the polymer.

The stabilizing effect of CNT-s can be also ascribed to the interfacial interaction between the nanofibres and PP increasing the activation energy of degradation and to retarding the degradation at the surface of the samples owing to the better heat distribution within the heat conductive CNT-containing samples. For a complete understanding of the difference between the performances of the two CNT types required, however, further experiments, as described in the hereafter.

Thermal scanning rheometry

Rheometry of varied temperature is suitable for evaluating the changes of the physical state of polymer systems under degradation. At lower temperature the curve is in connection with the flowing/dripping susceptibility of the polymers (important feature of fire retardancy), while at high temperature it can be used also for characterizing the consistency of the char formed after decomposition of the matrix.

The viscosity increasing effect of the nanotubes is apparent in the whole temperature range of the analysis. This effect is less pronounced in case of DWNT suggesting lower level of interfacial interaction probably due to lower level of dispersion. Comparing to virgin PP, which reaches the zero viscosity level slightly above 300°C, the nanotube containing samples preserve their consistency up to 400°C (Fig. 6.). At about this temperature, when the virgin PP is decomposed entirely, the charring of nanocomposites becomes dominant. The curve of the two composite types run parallel up to 450°C, when the curve of DWNT composite declines, while that of MWNT increases further sharply suggesting extended char formation. Considering the thermogravimetry and Raman results of pure nanotubes, it can be concluded that the DWNT, which degradates intensively in static state only about 520°C decomposes completely under shear stress already at 480°C, thus the shear stress activates its degradation. MWNT, being more stable, forms a consistent protective char on the surface of the polymer. The difference between the shift in the TG curves of composites prepared using DWNT and MWNT (Figs 4 and 5) can be explained by the combined effect of thermal stability alterations and of the different level of interfacial interaction.

Analysis of the composition of the residue

The Raman method was used also for identification of the composition of char residue of PP+nanotube sys-

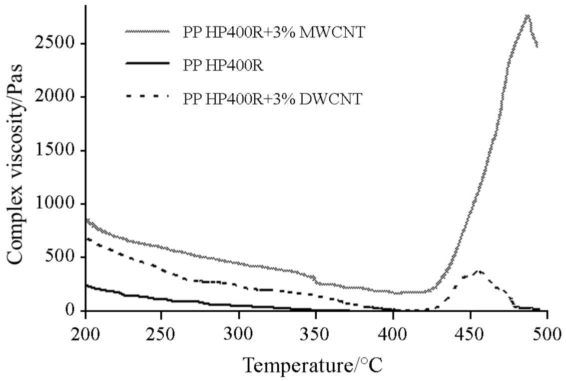

Fig. 6 Complex viscosity-temperature plots of PP and nanotube-PP nanocomposites

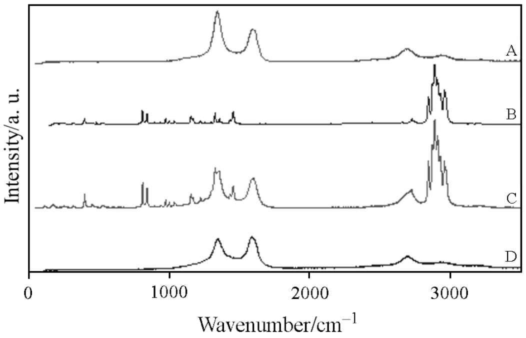

Fig. 7 A – Raman spectra of pure MWNT; B – pure polypropylene; C – PP-3%MWNT composite and D – PP-3%MWNT composite residue

tems. As Raman microscopy is a unique method for distinguishing the polymorph versions of carbon from each other, it could be used for chemical and morphological characterization of the char structure. Analyzing for example the residue of nanotube containing composites the char originating from the polymer and the nanotubes can hardly be distinguished by any other method.

This advantage initiated the utilization of the Raman system for determining the influence of nanotubes types on the composition of residue. Double-wall carbon nanotube (DWNT) and multi-wall carbon nanotube (MWNT) containing nanocomposites (PP HP400R, PP HP400R+3% DWNT and PP HP400R+3% MWNT resp.) and PP as reference were exposed to heat and shear stress in rheometer up to 500°C. No residue remained after the treatment of PP and PP-DWNT samples; however, considerable char remained after the pyrolysis of MWNT containing sample. According to Fig. 7, in which the pure PP, MWNT, their composite and the residue of the composite after treatment at 500°C is compared. The characteristic peaks of the residue overlap perfectly with those of pure MWNT. It means that the residue consists of MWNT of high thermal stability.

The single difference in the residue spectrum comparing to MWNT is that the D band at 1340 cm^{-1}, representing the disordered carbon components of the sample, decreased considerably. It suggests the decomposition of the amorphous part owing to the effect of fire, while the MWNT of perfect structure remained unchanged. The result suggests a good recyclability of this valuable component decreasing the cost of the composite.

Conclusions

The results of this study promote the understanding of the roles of carbon nanotubes in thermal stability of polypropylene composites. Two types of CNT were characterised by thermal analysis indicating the higher thermal stability of MWNT than the DWNT. The Raman microscopy observation revealed that moderate irreversible changes take place, already below the decomposition temperature which could be monitored by D band of the CNT. This observation suggests that the disordered (mainly amorphous) part of sample burnt out left behind a more purified nanotubes. The TG results of PP-CNT composites indicated the thermal stability increasing effect of nanotubes, which is more considerable in case of MWNT and under air atmosphere than for DWCNT and inert atmosphere. The significant role of MWNT in the increase of the thermal stability of PP based composites was confirmed by thermal scanning rheometry as well, which pointed out also the effect shear stress in the stability of CNT-s. Raman study of the composition of the residue allowed identifying the CNT part in the char, which was found to be dominant and surprisingly pure comparing to the original additive.

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