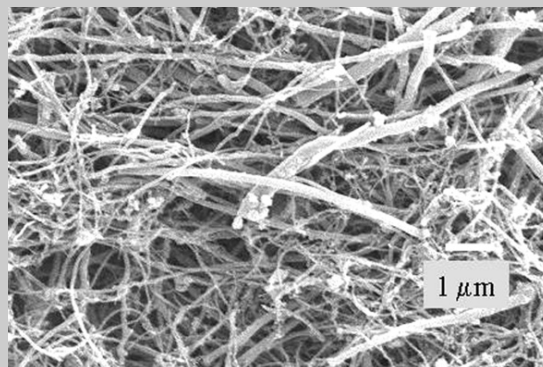


Communication: Nanocomposites based on poly(propylene) and multi-wall carbon nanotubes (up to 2 vol.-%) were melt blended, yielding a good dispersion of nanotubes without using any organic treatment or additional additives. Carbon nanotubes are found to significantly enhance the thermal stability of poly(propylene) in nitrogen at high temperatures. Specifically, the nanotube additive greatly reduced the heat release rate of poly(propylene). They are found to be at least as effective a flame-retardant as clay/poly(propylene) nanocomposites.

SEM photomicrograph of MWNT dispersion in the poly(propylene) composite after solvent removal.



Thermal Degradation and Flammability Properties of Poly(propylene)/Carbon Nanotube Composites

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Introduction

There is a high level of interest in using nanoscale reinforcing fillers for making polymeric nanocomposite materials with exceptional properties.^[1,2] (Nanocomposites are particle-filled polymers where at least one dimension of the dispersed particle is on the nanometer scale.) An improvement in flammability properties of polymers has been obtained with nanoscale additives and these filled systems provide an alternative to conventional flame retardants. It is important to explore how the asymmetry (aspect ratio) and other geometrical effects of nanoparticle additives influence the flammability properties of polymer nanocomposites. At present, the most common approach is the use of layered silicates having large aspect ratios; the flame retardant (FR) effectiveness of clay/polymer nanocomposites with various resins has been demonstrated.^[1–6] The FR effectiveness in poly(methyl methacrylate) (PMMA) of nanoscale silica particles (average diameter of 12 nm) has also been demonstrated.^[7] Carbon nanotubes provide another candidate as

an FR additive because of their highly elongated shape, but we are aware of only one study concerned with an ethylene vinyl acetate (EVA)/carbon nanotube nanocomposites.^[8] Polyolefins are quite flammable and it is difficult to reduce their heat release rates with environmentally friendly flame retardants. Thus, we have investigated the effects of the addition of a small quantity of carbon nanotubes on the flame retardant behavior of poly(propylene) (PP). Characteristics of carbon nanotubes and of some nanotube-based polymer composites are well summarized in a previous publication.^[9] Moreover, nanotube-based composites can be made with various resins.^[10–12]

Multi-wall carbon nanotubes (MWNTs) are used due to their cost advantage over single wall carbon nanotubes. There are two practical advantages for dispersing carbon nanotubes in PP compared with dispersing clay or silica into polyolefins. Since clay and silica are hydrophilic, they often require (i) an organic treatment on their surfaces and/or (ii) a compatibilizing polymer modifier, e.g. PP grafted with maleic anhydride (PP-g-MA).^[13] How-

ever, carbon nanotubes are organophilic and can be dispersed directly into the polymer.

Experimental Part

MWNTs were made using xylene as a carbon source and ferrocene as catalyst at about 675 °C.^[14] Composites were prepared by melt blending the MWNT/PP mixture in a Haake PolyLab shear mixer.^a The mixer temperature was raised to 180 °C, and PP pellets (Grade 6331, Montell Polyolefins) were added with a mixer rpm of 20. The pellets melted in about 3 min, and the mixer torque approached a constant value in about 5 min. MWNTs were added at this time and mixing was continued for 30 min. All samples were compression molded at 190 °C under a pressure of 6 metric tons to make 75 mm diameter by 8 mm thick disks. Thermal gravimetric analyses (TGA) were conducted using a TA Instruments SDT 2960 at 10 °C/min from 25 °C to 800 °C in nitrogen and in air. The standard uncertainty on sample mass measurement is $\pm 1\%$. The samples (≈ 5 mg) were placed in open ceramic pans. An Atlas Cone 2 was used to carry out measurements of flammability properties following the procedure defined in ASTM E 1354-90. Our procedure involved exposed specimens wrapped with aluminium foil except the top surface in a horizontal orientation at an external radiant flux of 50 kW/m². This flux corresponds to typical heat fluxes in a medium size fire. The standard uncertainty of the measured heat release rate is $\pm 10\%$.

Morphologies of the nanotubes in the melt blended material and in the combustion samples were evaluated using scanning electron microscopy (SEM; Hitachi 3200N) and energy dispersive scattering (EDS) for composition (Noran). Polymer was removed from unburned samples by heating them in excess 1,2,4 trichlorobenzene to 160 °C, at which point the PP crystallites melted, and dissolved into the solvent. The nanotubes were recovered from the suspension by hot filtration and were dried. The nanotube morphology of the burned samples was investigated using SEM directly and after dispersion in alcohol with ultrasonication.

Results

An SEM picture of the recovered MWNTs from the unburned PP/MWNT (2 vol.-%) sample by the procedure described above is shown in Figure 1. It shows well dispersed MWNTs implying good dispersion in the PP/MWNT nanocomposite. Normalized sample mass loss rate divided by the heating rate measured by TGA for the three samples is plotted in Figure 2a. These results show that PP degrades with a large single peak starting around 300 °C in nitrogen. This large peak corresponds to the thermal degradation of PP initiated primarily by thermal scissions of C—C chain bonds accompanied by a transfer of hydrogen at the site of scission.^[15] The results of the

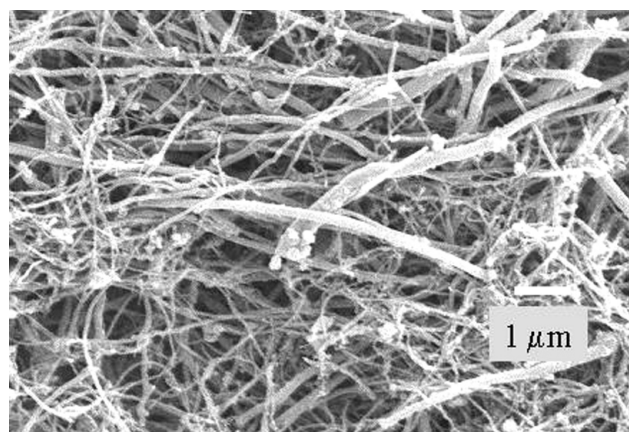


Figure 1. SEM photomicrograph of MWNT dispersion in the poly(propylene) composite after solvent removal.

PP/MWNT samples also show broad single peaks, but the temperatures at the peak sample weight loss rates are about 12 °C higher than that of PP. The amount of MWNTs in PP does not make a significant enhancement in thermal stability of this nanocomposite system in nitrogen for the range investigated in this study. An increase in the temperature at the peak sample mass loss rate is also reported for the PP/PP-g-MA/clay system compared with PP/PP-g-MA.^[16] This previous investigation indicated an increase of 17 °C with 10 wt.-% of clay in PP/PP-g-MA. This effect was attributed to a barrier labyrinth effect of the clay platelets so that the diffusion of degradation products from the bulk of the polymer to the gas phase is slowed down. The temperature increase observed in the present study could arise from a similar barrier effect due to the hindered transport of degradation products caused by the numerous carbon tubes in the sample.

Thermal degradation of the three samples in air is significantly different from that in nitrogen. The thermal stability of PP in air is prominently reduced by oxidative dehydrogenation accompanied by hydrogen abstraction^[16] and a broad mass loss rate peak is observed around 298 °C, as shown in Figure 2b. The thermal stability of the PP/MWNT nanocomposites appears to be more complex than that of PP. The mass loss of the PP/MWNT nanocomposites starts around 205 °C. The nanocomposites are less stable than PP at this temperature range. However, above 250 °C, they become more stable than PP. Sharp peaks are shown above 340 °C for the PP/MWNT samples in Figure 2b. The observed complex thermal stability behavior of the PP/MWNT is significantly different from that of the PP/PP-g-MA/clay samples.^[16] The thermal stability of the latter samples is much better than that of PP and does not generate the multiple peaks shown in Figure 2b. This complex thermal stability behavior of the PP/MWNT nanocomposites could be caused by a small amount of iron in the MWNTs used in this study. It is reported that iron particles are formed

^a Certain commercial equipment, instruments, materials, services or companies are identified in this paper in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

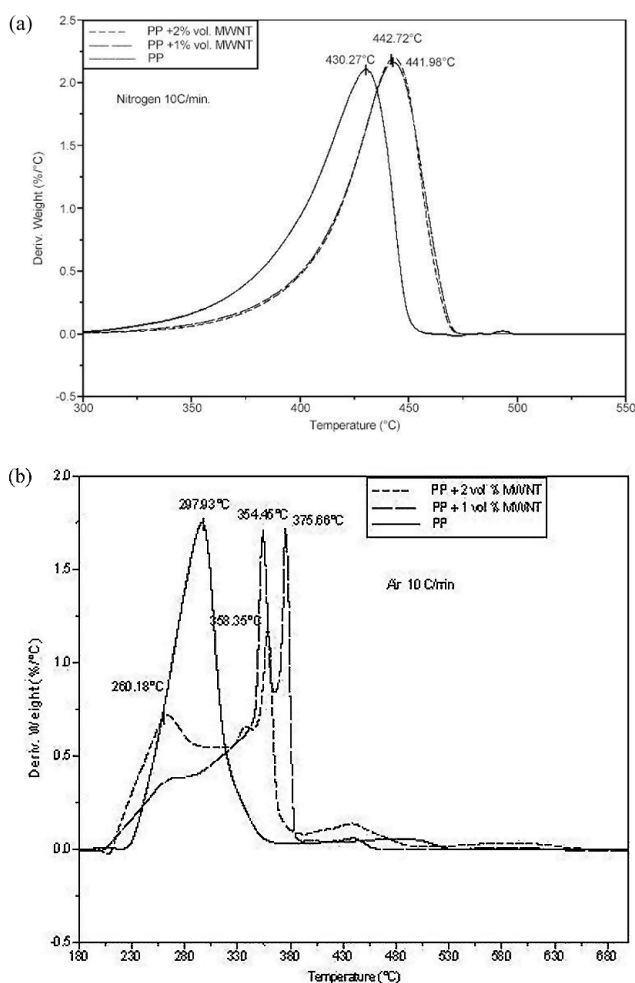


Figure 2. TGA analyses of normalized mass loss rate by the initial sample mass at a heating rate of 10 °C/min in (a) nitrogen and (b) air.

from ferrocene used as a catalyst to make MWNTs. The iron content in MWNTs is 7.1 wt.-%.^[17] The iron particles are encapsulated at various locations inside the nanotubes, and also as nanospheres near the nanotube tips. Nanotube tips are visible in Figure 1 and are the nodules at the end of some of the tubes. Nanoparticulate iron is pyrophoric, and could reduce the thermal oxidative stability of MWNTs,^[18] acting as a catalyst during the oxidative degradation of the PP/MWNT nanocomposites. Iron particles could form iron oxides during thermal degradation and iron oxides have been used as flame retardant additives to various polymers.^[19,20] Furthermore, it was reported that radical trapping by the iron within the clay enhanced the thermal stability of polystyrene (PS) in PS/clay nanocomposites.^[21] However, the same study found that iron did not affect the thermal stability of PS in PS/iron-containing graphite nanocomposites. Since the iron particles are inside and at ends of the MWNTs, their contact with PP chains during the TGA experiment would be minimal and would not occur until the walls of the nano-

tube tip were catalytically degraded. If this were so, the role of iron particles in MWNTs might not be important for the thermal stability of the PP/MWNT nanocomposite. However, without further study, the role of iron particles in MWNTs in the thermal degradation of the PP/MWNT nanocomposite is not clear. We plan to explore this by studying the thermal stability of the PP/MWNT nanocomposites without iron particles. These can be eliminated by annealing MWNTs at a high temperature.^[18]

A comparison of heat release rate curves among the three samples is shown in Figure 3. The results show that the heat release rates of the PP/MWNT nanocomposites are much lower than that of PP even though the amount of MWNTs in PP is quite small. The peak heat release rates of the PP/MWNT nanocomposites are about 27% (1 vol.-%) and 32% (2 vol.-%) of that of PP. The time-averaged heat release rates over the burning time are about 53% (1 vol.-%) and 58% (2 vol.-%) of that of PP. The effects of the content level of MWNTs in PP used in this study do not appear to cause any significant reduction in heat release rate. The total heat release, the integral of the heat release rate curve over the duration of the experiment, is about the same for the three samples. The curves of the mass loss rate per unit surface area for the three samples are very similar to those of the heat release rate. Since the specific heat of combustion value is calculated by dividing measured heat release rate with measured mass loss rate, this indicates that the specific heat of combustion is about the same for the three samples. The calculated specific heat of combustion of each sample is 43

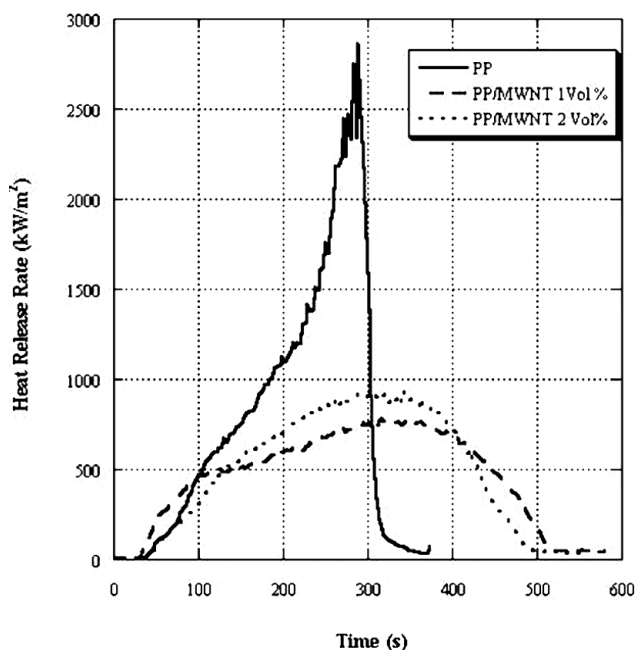


Figure 3. Heat release rate curves of the three samples at 50 kW/m².

± 1 MJ/kg. The above results indicate that the PP/MWNT nanocomposites burn much slower than PP but they all burn nearly completely. These observations are similar to those made with clay/nanocomposites^[2,3] and with composites made by the addition of nanoscale silica to PMMA.^[7] This indicates that the observed FR performance of the PP/MWNT nanocomposite is mainly due to chemical or/and physical processes in the condensed phase instead of in the gas phase. The residues were collected at the end of the test (after additional two minutes exposure after flame out) in a cone calorimeter. A small quantity of the residue (0.2% (for 1 vol.-% sample) and 1.6% (for 2 vol.-%) of the initial mass) was left in the sample container at the end of the test for the PP/MWNT nanocomposites.

There was more residue left for both samples at the end of flaming combustion than at the end of the test, but glowing combustion (surface oxidative combustion) consumed some of the residues during the two minutes non-flaming exposure. The PP sample did not leave any residue as expected, but the PP/MWNT (1 vol.-%) nanocomposite left mainly reddish residue also with a small amount of black structurally diffusive (“fluffy”) residue. An SEM picture of the residue of the PP/MWNT (1 vol.-%) nanocomposite shows partially oxidized carbon nanotubes embedded in an agglomerate composed of iron oxide primary particles. EDS analysis of the reddish residue shows strong signals of Fe and O, which indicates that the residue is mainly iron oxide. Carbon nanotubes were mainly consumed by the two minutes of glowing combustion and mainly iron oxides were left. The PP/MWNT (2 vol.-%) nanocomposite left a significant amount of the black fluffy residue in conjunction with the reddish residue. The black fluffy residue mainly consists

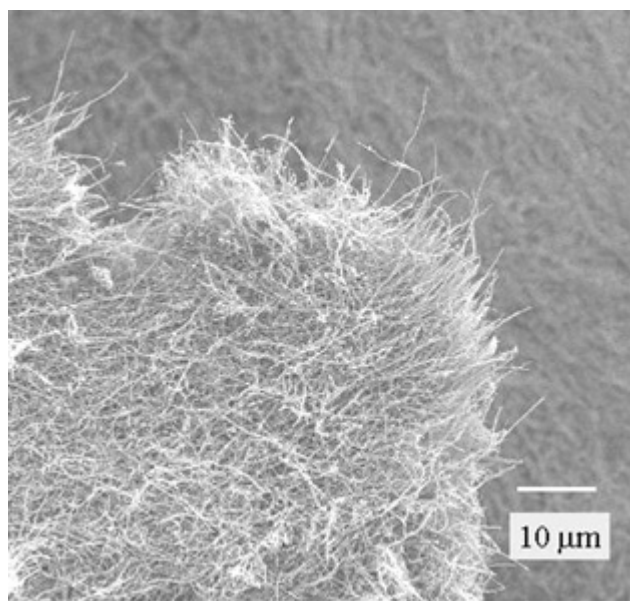


Figure 4. SEM picture of the black fluffy residue of PP/MWNT (2 vol.-%).

of locally aligned carbon tubes (Figure 4). EDS analysis of the black fluffy residue shows essentially no iron present along with low oxygen levels in the material.

Discussion

This exploratory study indicates that the presence of nanotubes in PP/MWNT nanocomposites modifies thermal and oxidative degradation processes of PP and also significantly reduces the heat release rate of PP. Their reduction in heat release rate of PP is at least as much as for PP/PP-g-MA/clay nanocomposites.^[3] A similar observation has been found for the FR performance of EVA with dispersed MWNTs compared to the EVA/clay nanocomposite.^[8] Notably, the amount of MWNTs added to PP does not appear to significantly affect the peak heat release rate for the concentration range investigated in the present study (1–2 vol.-% corresponds to about 2–4 wt.-%). For clay/polymer nanocomposites, the heat release rate decreases with the level of clay content roughly up to 5 wt.-%. It was proposed for the clay/polymer nanocomposites that the reduction in heat release rate was due to the formation of a protective surface barrier layer consisting of accumulated clay platelets with a small amount of carbonaceous char.^[3,22] Another FR mechanism proposed by Wilkie et al. is radical trapping of paramagnetic iron within the clay.^[21] They showed that even when the fraction of clay was as low as 0.1%, the peak heat release rate of the clay/PS nanocomposite is lowered by 40%, a value not much different from that observed at higher amounts of clay. In our study, the accumulation of carbon tubes with a network structure is observed as shown in Figure 4. The formation of the network tends to increase the mechanical integrity of a protective layer which could act as a thermal insulation layer and also a barrier for evolved degradation products to the gas phase.^[23] However, our PP/MWNT nanocomposites contain a small amount of iron compounds. A possible role of iron particles in MWNTs is the formation of iron oxides during combustion. Iron oxides were used as an FR additive for certain resins.^[19,20] It is notable that the purity of MWNTs has little effect on the heat release rate for the EVA/MWNT samples,^[8] although the purification procedure of the MWNTs was not discussed in detail. At present, either FR mechanism described above appears to explain the observed experimental results of the PP/MWNT sample, but we cannot determine which mechanism applies to the PP/MWNT sample studied here without further study. We plan to measure thermal and flammability property measurements of PP/MWNT samples containing no iron particles to clarify the role of iron.

The results show great potential for the use of carbon nanotubes as a flame retardant additive for polymer materials. In particular, the carbon nanotubes seem to be well

suiting for non-polar resins such as polyolefins because the dispersion of carbon nanotubes seemed to be much easier than dispersing clays since the former do not require organic treatment and the use of a compatibilizer. The only drawbacks for the use of carbon nanotubes are the black color of the compounded system and their costs. However, the cost of the carbon nanotubes will become much lower as the level of production increases significantly.

Conclusion

Poly(propylene)/multiple-wall carbon nanotube nanocomposite samples were prepared with good dispersion of the nanotubes without any organic treatment of the nanotube surfaces or/and the use of a compatibilizer. MWNTs enhance the thermal stability of PP in nitrogen and also in air except around 205 °C (at heating rate of 10 °C/min) where they reduce the oxidative thermal stability. MWNTs significantly reduce the heat release rate of PP and are at least as FR effective as PP/PP-g-MA/clay systems. The accumulation of carbon nanotubes and iron oxides were observed in the sample residues collected at the end of the test conducted in a cone calorimeter.

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