

Synergistic Effect of Carbon Nanotubes on the Flame Retardancy of Poly(methyl methacrylate)/Zinc Oxalate Nanocomposites

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Received April 3, 2016; Revised May 31, 2016; Accepted June 3, 2016

Abstract: Carbon nanotubes have incorporated in poly(methyl methacrylate) (PMMA) nanocomposites as a synergist of zinc oxalate nanoparticles in order to enhance the flame retardancy. PMMA nanocomposites filled with the newly developed environmentally friendly zinc oxalate nanoparticles and with multi-walled nanotubes (MWNTs), both serving as flame retardants, were prepared by applying the solution blending method. The fire behavior of these composites was systematically studied by carrying out limiting oxygen index (LOI) and pyrolysis combustion flow calorimetry (PCFC) tests. The introduction of MWNTs into the PMMA/zinc oxalate nanocomposites improved the LOI values and markedly decreased the peak heat release rate. It can be suggested that this improvement in the flame retardancy resulted from the formation of stable protective char layers during the combustion process.

Keywords: poly(methyl methacrylate), nanocomposites, flame retardancy, zinc oxalate, multi-walled nanotube (MWNT).

Introduction

Poly(methyl methacrylate) (PMMA) is an important amorphous thermoplastic with desirable properties, including advantageous optical properties (such as clarity, and transparency from the near ultraviolet to the near infrared), chemical resistance, good formability and moldability, high strength and dimensional stability.^{1,2} Moreover, PMMA displays good resistance to both acidic and alkaline environments, and is resistant to many inorganic reagents, aliphatic hydrocarbons, and non-polar solvents.³ It is also extraordinarily resistant to oxidative photodegradation and hence to sunlight, and exhibits unusually good weathering behavior.^{3,4} Therefore, PMMA has the potential to be the material of choice for outdoor applications. However, one major problem associated with the application of PMMA is its inherently poor thermal stability at high temperatures. As a result, it is a flammable material that upon combustion produces a large quantity of monomers and that needs to be reinforced with flame retardants.

Brominated flame retardants are the most effective flame retardants in the market and have been largely adopted in the plastics engineering fields.⁵ However, halogen flame retardants can release toxic gases when they are exposed to high temperatures.⁶ Halogen-free, environmentally friendly flame retardants that do not release toxic gases have recently been

developed. Metallic hydroxides constitute one of the most promising types of halogen-free flame retardants.⁷⁻¹⁰ However, since the decomposition temperatures of metallic hydroxides are generally lower than processing temperatures, their applications as flame retardants in the commercial processes are limited.¹¹

In this study, a newly developed environmentally friendly flame retardant, consisting of zinc oxalate nanoparticles, was introduced into the PMMA polymer. However, the relatively low percentage of Zn in zinc oxalate results in the generation of a relatively low content of zinc oxide in its char residue, and its ability to form stable protective char layers is poor. As shown previously, the formation of char is very important in promoting flame retardancy because of its barrier properties:^{12,13} a char layer preserves the polymer by covering it and hence interfering with its direct contact with oxygen in the air, and in this way acts as a heat shield to slow the thermal degradation of the polymer. Therefore, zinc oxalate nanoparticles need to be supplemented with another flame retardant to improve the process of char formation during decomposition.

Filler nanostructures with a high aspect ratio such as nanoclay, extended carbon nanostructures, and layered double hydroxide have a high probability to enhance char formation and achieve synergistic improvements in flame retardancy of the polymer filled with zinc oxalate nanoparticles.^{14,15} Among them, carbon nanotubes (CNTs) are commonly used as filler to improve the mechanical and electrical properties of nanocomposites. Since nanoclay and layered double hydroxide are hydrophilic,

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they require an organic treatment on their surfaces for the polymer to penetrate easily into the layers. However, CNTs are organophilic and can be dispersed directly into the polymer.¹⁶ Several researchers have recently reported markedly better thermal stabilities for polymer/CNT nanocomposites than for the virgin polymer, and percolated CNT network structures have shown promising formation of char layers during burning tests, without producing any major cracks or openings.¹⁶⁻¹⁹

The current study explored whether CNTs incorporated in PMMA/zinc oxalate nanoparticles nanocomposites can act synergistically as flame retardants. PMMA nanocomposites containing multi-walled nanotube (MWNTs) and zinc oxalate nanoparticles were prepared by using the solution blending method. A variety of technical approaches were employed to characterize the flammability of the nanocomposites, and a plausible association between the addition of MWNTs and improved fire retardancy was shown.

Experimental

Materials. The matrix polymer used in this study was poly (methyl methacrylate) (PMMA) (HP05 grade; melt flow index 1.6 g/10 min (230 °C, 3.8 kg); density 1.18 g/cm³), which was purchased from LG MMA Company (Republic of Korea). Zinc acetate and oxalic acid were purchased from Aldrich (USA), and were used without further purification. MWNT was produced by Cheil Industries Inc. (Republic of Korea). The *N,N*-dimethyl formamide (DMF) used in the solution blending was a product of Aldrich (USA).

Preparation of Zinc Oxalate. In a typical synthesis, 50 mL of a 1 M aqueous zinc acetate solution was heated at 70 °C in an Erlenmeyer flask with magnetic stirring. And 50 mL of 1 M aqueous oxalic acid was prepared and poured into the zinc acetate solution, and the resulting mixture was stirred vigorously for 30 min to yield zinc oxalate complexes. Then, the precipitate was filtered and washed three times with deionized water (70 °C). The product was kept in a vacuum oven at 60 °C for 24 h.

Fabrication of PMMA Nanocomposites. Using the solution blending method, *N,N*-dimethylformamide (DMF) was chosen to dissolve the PMMA polymer and to form a dispersion of the MWNTs *via* use of bath sonication for 12 h. To obtain a good nanotube dispersion, it was critical to select an appropriate concentration of the nanotube in DMF. Prior to dissolving PMMA, a mass of 0.025 g MWNTs was dispersed in 125 mL of DMF by using bath sonication for 12 h. A mass of 5 g of PMMA was then dissolved in this MWNT solution with vigorous stirring for 10 h, followed by addition of 0.415 g of the prepared zinc oxalate to the PMMA/MWNT solution and subsequent sonication for 3 h. Finally, the resulting PMMA/MWNT/zinc oxalate solution was dried under vacuum at 120 °C for one day.

Analysis and Characterizations. Images of the surface morphology of the nanocomposites were obtained using scan-

ning electron microscopy (SEM; JEOL JSM 6700F, Japan). The samples for the SEM measurements were placed on carbon surfaces and then coated with Pt. The X-ray diffraction (XRD) analysis was performed using a D/Max RB (4kW). An acceleration voltage of 40 kV and 45 mA was applied using CuK α radiation. The thermal properties of the zinc oxalate nanoparticles were investigated using a differential scanning calorimeter (DSC, TA Instruments, USA). The flame retardancy was first evaluated by carrying out limiting oxygen index (LOI) tests. The LOI values were calculated by using an oxygen index meter (Fire Testing Technology). The flame retardancy of the sample was finally evaluated by carrying out tests using a pyrolysis combustion flow calorimeter (PCFC, Fire Testing Technology Ltd., UK) to calculate heat release rates (HRRs). The samples were pyrolyzed to 415 °C in N₂ at a heating rate 1 °C/s and combusted at 600 °C. Each type of sample was tested at least five times and the results were averaged.

Results and Discussion

Oxalate complexes are coordination compounds produced by a chemical reaction of an oxalic acid with a transition metal such as zinc (Zn). The chemical formula of the oxalate anion is C₂O₄²⁻, and its structural formula is shown in Figure 1(A). The distribution of the charge on oxalate allows it to act as a chelator of various positively charged metal ions. Metal oxalates are environmentally friendly, safe halogen-free flame retardants and smoke suppressants with numerous benefits:

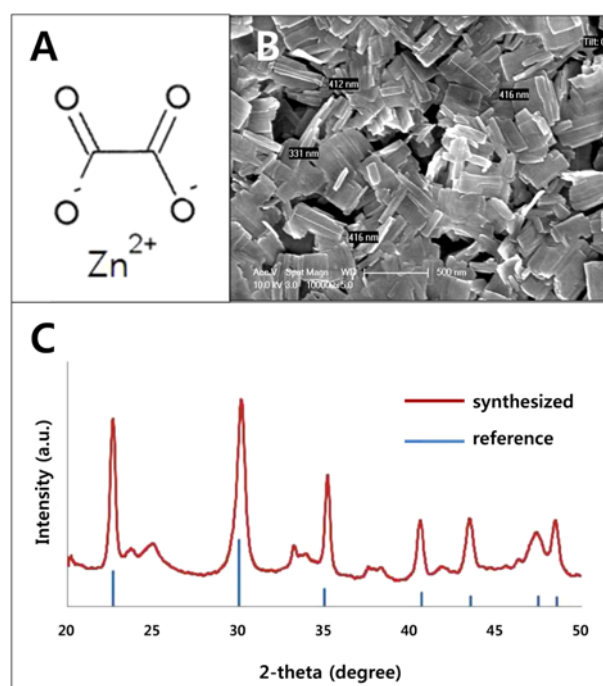


Figure 1. (A) The structural formula of the zinc oxalate complex. (B) SEM image and (C) powder X-ray diffraction pattern of the zinc oxalate nanoparticles.

for example, they neither involve the elimination of heavy metal promoters nor do they generate toxic fumes.²⁰ The flame retardancy mechanism of metal oxalates is based on its thermal decomposition between 400 °C and 500 °C. The decomposition of the metal oxalate is endothermic, which cools the polymer. During this endothermic reaction, metal oxalate releases carbon monoxide (CO) and carbon dioxide (CO₂).^{20,21} As these gases build up near the surface of the decomposing material, they displace and hence lower the concentration of oxygen and burnable gases. Zinc oxalate loses about 47% of its mass as CO and CO₂ when heated to the temperatures above 400 °C.²²

The zinc oxalate nanoparticles were produced by modifying a water-based protocol described previously.²³ The key to achieving high yields and mono-dispersity involved promoting the formation of seed particles and then controlling the reaction kinetics. Figure 1(B) shows the detailed morphologies of the synthesized zinc oxalate nanoparticles. The synthesized zinc oxalate was observed to form nanorods, with an average diameter of 180 nm and length of 400 nm, and hence an aspect ratio of *ca.* 2.2:1. The X-ray diffraction (XRD) pattern recorded from the sample is displayed in Figure 1(C). All of the reflections in the pattern could be indexed on the basis of a monoclinic cell reported for zinc oxalate dihydrate (JCPDS # 25-1029).²⁴ DSC analysis of these zinc oxalate nanoparticles showed two endothermic peaks (see Figure S1). The first endothermic peak occurred at about 150 °C, which corresponded to the conversion of zinc oxalate dihydrate to anhydrous zinc oxalate with the loss of two water molecules. The second endothermic peak occurred at about 400 °C, indicating the conversion of anhydrous zinc oxalate to zinc oxide and the resulting release of carbon monoxide and carbon dioxide. These results indicated that we produced monodisperse zinc oxalate nanoparticles that can be used as flame retardants.

The prepared zinc oxalate nanoparticles were well dispersed in various organic solvents including acetone, and the nanoparticles were uniformly dispersed in the acetone solution of PMMA by carrying out sonication for 3 h. Table SI summarizes the limiting oxygen indices (LOIs) of the preliminarily formed PMMA/zinc oxalate nanocomposites with different weight fractions. Oxygen index methods, which describe the tendency of a material to sustain a flame, are widely used as a tool to investigate the flammability of polymers.^{25,26} They in fact provide a convenient and reproducible means of determining a numerical measure of flammability. Neat PMMA used in the present study was observed to have a quite low LOI of 18.0%. The LOI value was slightly improved with the incorporation of the zinc oxalate nanoparticles. PMMA composites consisting of 16.0 wt% zinc oxalate nanoparticles showed an LOI of 20.6%, which is nearly in the non-flammable region. Since the aim of the present study was to evaluate the potential synergistic flame retardancy action of carbon nanotubes, when used in combinations with a new flame-retardant in PMMA, the concentration of the zinc oxalate nanoparticles in the final PMMA nanocomposites was fixed at 8.0 wt%.

PMMA nanocomposites containing MWNTs and zinc oxalate were prepared by using the solution blending method, with *N,N*-dimethylformamide (DMF) chosen as the organic solvent. To obtain a uniform dispersion of MWNTs in DMF, selecting the appropriate MWNT concentration is critical.¹⁶ In the organic solvent, the average nanotube bundle diameter was found to increase as the nanotube concentration was increased, and the agglomerated nanotubes were observed by the naked eye when the initial nanotube concentration was greater than 0.2 mg/mL. At 0.2 mg/mL, the suspension was visually homogeneous, which indicates that the nanotubes in the prepared PMMA/MWNT composite in solution state were well dispersed into the polymer matrix. Therefore, we chose to use 0.2 mg/mL MWNT, which is nearly 0.5 wt% of the matrix polymer, PMMA.

The distributions of MWNTs and the zinc oxalate particles in the nanocomposites were examined using scanning electron microscopy (SEM). SEM images at different magnifications are shown in Figure 2. The average size of the zinc oxalate particles, shown in Figure 2(A), was observed to be approximately 2 μm, suggesting the presence of large and unevenly dispersed secondary particles in the nanocomposites. However, primary particles with dimensions of approximately 150-200 nm were also observed in the nanocomposites, as shown in the magnified image in Figure 2(B). Figure 2(B) also shows the MWNTs present in the form of bundles and ropes due to the relatively strong van der Waals interactions between the individual nano-

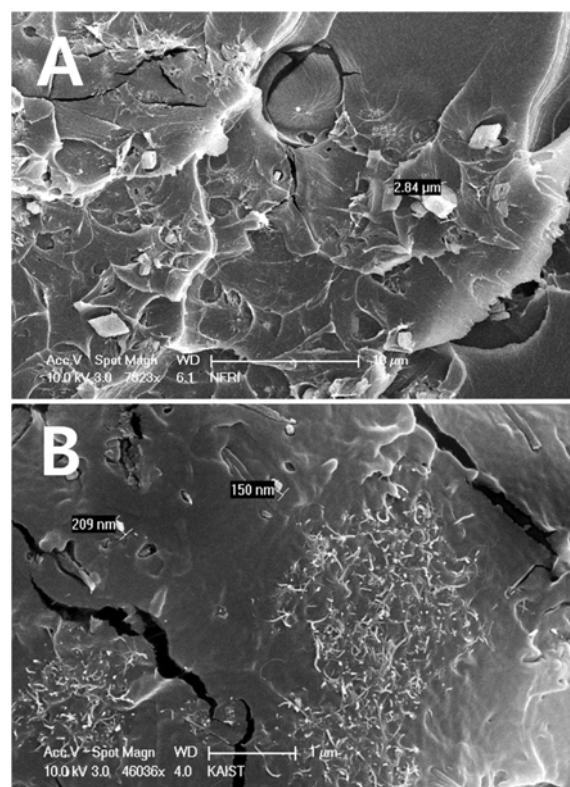


Figure 2. SEM images of MWNT/zinc oxalate/PMMA nanocomposites at (A) low magnification and (B) high magnification.

tubes, hence showing that the PMMA nanocomposites contained well-dispersed bundled nanotubes embedded in the PMMA matrix.¹⁴

The effects of adding zinc oxalate nanoparticles and MWNTs individually to the PMMA on the LOI of the composite are summarized in Table SII. The LOI was improved to a value of 19.7% by the addition of 8.0 wt% zinc oxalate nanoparticles, but only to 18.9% by the addition of 0.5 wt% MWNT. This index was improved most, to a value of 20.3% when CNT and zinc oxalates were added together. Although the LOI results correlated well with the results of other practical testing methods such as UL 94, LOI results are known to be generally unreliable at predicting real fire performances in most cases. LOI is determined using a downward burning configuration, which has different burning rate and heat transfer characteristics than do most real fires.²⁷ Moreover, the LOI is measured for the most part in an environment with an oxygen concentration higher than that in the atmosphere.

The heat release rate (HRR) has been demonstrated to be the most significant parameter for characterizing flammability behaviors, and for evaluating and predicting fire hazards of flammable materials.²⁷ Pyrolysis combustion flow calorimeters (PCFCs, also referred to as a micro-scale combustion calorimeters) have a dynamic capability to measure HRR using only a few milligrams of a sample, based on the amount of oxygen consumed in a non-flaming oxidation process.²⁸ We therefore investigated the flammability properties of PMMA/zinc oxalate/MWNT nanocomposites by using a PCFC. The HRR vs. temperature curves of pure PMMA and of the PMMA nanocomposites are shown in Figure 3.

Adding 8.0 wt% zinc oxalate nanoparticles to the PMMA matrix was observed to lower the peak heat release rate (PHRR) approximately 8.2%, while adding 0.5 wt% MWNTs reduced the PHRR by 7.7%. When both the zinc oxalate nanoparticles (8.0 wt%) and MWNTs (0.5 wt%) were together incorporated into the PMMA matrix, a dramatic decrease in the PHRR was observed, by 31.1%. These results provided evidence

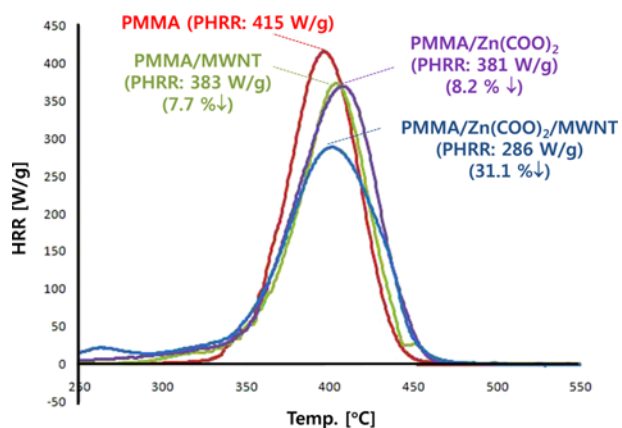


Figure 3. HRR vs. temperature curves of pure PMMA and PMMA nanocomposites incorporated with MWNTs and/or zinc oxalate nanoparticles.

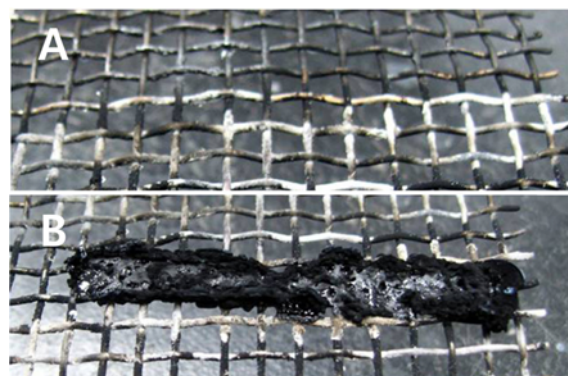


Figure 4. Pictures of the fire residues from (A) the PMMA/zinc oxalate nanocomposites and (B) the PMMA/MWNT/zinc oxalate nanocomposites.

for MWNTs and zinc oxalate nanoparticles acting synergistically to improve the flame retardancy of PMMA nanocomposites.

The fire residues from PMMA nanocomposites with and without MWNTs were compared, as shown in the photographs in Figure 4. Little residue remained in the specimen holder after combustion of the PMMA/zinc oxalate composite. As described above, the relatively low percentage of Zn in zinc oxalate results in the generation of a relatively low content of zinc oxide in its char residue, which does not favor the formation of the char. When burning the PMMA nanocomposite filled with zinc oxalate and MWNTs, however, MWNTs apparently formed a thin, continuous and crack-free network on the sample surface. Formation of a uniform CNT layer is the key point of using nanocomposites containing MWNT for enhancing fire retardancy.

A fire-retardancy mechanism based on the synergistic actions of the MWNTs and zinc oxalate nanoparticles is proposed in Figure 5. According to this mechanism, our polymers began to burn when heated to temperatures at which thermal degradation begins, and the degradation products became superheated and nucleated to form bubbles, which then burst at the heated surfaces, discharging their contents as fuel vapor into the gas phase.¹⁵ The force of numerous rising bubbles during combustion according to this mechanism pushed the MWNTs

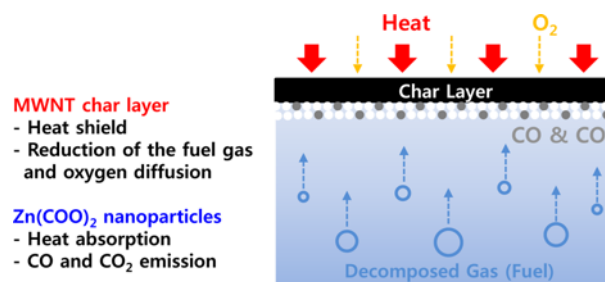


Figure 5. Schematic illustration showing the synergistic effects of the MWNTs and zinc oxalate nanoparticles on the flame retardancy of PMMA nanocomposites.

to the surface of the material, leading to the formation of a nanotube network layer. This layer, we suggest, acted as a barrier against the transmission of gas from the decomposed bulk polymer and against the diffusion of oxygen from the air into the material.²⁹ In parallel with the action of the MWNTs, the zinc oxalate accordingly to this mechanism was converted into zinc oxide as a result of the endothermic deposition of the metal oxalate when the polymers began to burn. During this endothermic reaction, metal oxalate absorbed heat and released CO and CO₂ near the compound surface, according to our proposal, with these released gases displacing and lowering the local concentration of oxygen and burnable gases. By these combined effects, MWNTs and zinc oxalate nanoparticles could act synergistically as flame retardants.

Conclusions

MWNTs have been introduced into PMMA/zinc oxalate nanocomposites and acted together with the zinc oxalate nanoparticles to synergistically improve the flame retardancy of the polymer nanocomposite. The PMMA nanocomposites containing MWNTs and zinc oxalate were prepared by solution blending, and fine dispersions of the additives in the polymer matrix were produced by vigorous stirring and sonication. The incorporation of MWNTs into the PMMA/zinc oxalate nanocomposites improved the LOI values and markedly decreased the peak heat release rate. This improvement may have resulted from the migration of the MWNTs to the composite surface to form stable protective char layers after the combustion process. This study not only advances our understanding of the role played by MWNTs as flame retardants for polymers but also allows us to develop a system of promising environmentally friendly flame retardants.

Acknowledgments. This work was supported by the National Research Foundation of Korea (KRF) grants funded by the Ministry of Science, ICT & Future Planning (MSIP) of Korea under contact no. NRF-2015R1C1A1A02036649.

Supporting Information: Information is available regarding the LOI values of the nanocomposites, and differential scanning calorimetry (DSC) thermogram of the zinc oxalate nanoparticles. The materials are available *via* the Internet at <http://www.springer.com/13233>.

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