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Fire retardancy of emulsion polymerized poly (methyl methacrylate)/cerium(IV) dioxide and polystyrene/cerium(IV) dioxide nanocomposites

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ABSTRACT

In situ emulsion polymerization was employed to obtain poly (methyl methacrylate) (PMMA)/cerium(IV) dioxide and polystyrene (PS)/cerium(IV) dioxide nanocomposites at two different cerium(IV) dioxide loadings (2.3 wt% and 4.6 wt%). Transmission electron microscope results indicated uniform dispersion of cerium (IV) dioxide in the polymer matrix. Both PMMA and PS nanocomposites exhibit lower thermal stability than the pristine polymers. Microscale combustion calorimeter (MCC) and cone calorimetry are used to evaluate the fire retardancy of the polymer nanocomposites. PMMA/cerium(IV) dioxide showed significant heat release rate (HRR) reduction at low loadings (<5 wt%), while PS/cerium(IV) dioxide exhibits less HRR reduction at the same loadings. An explanation of the role of cerium (IV) dioxide in fire retardancy of polymer/ceria nanocomposites based on XPS results is suggested.

1. Introduction

Fire retardancy of polymer nanocomposites has been extensively investigated in the past decade [1]. In addition to the most studied nanomaterial, montmorillonite (MMT) system, other nanofillers have also attracted interest, including carbon nanotubes, layered double hydroxides, polyhedral oligomeric silsesquioxane (POSS), and metal oxides [1–4]. Metal oxides, mostly transition metals, usually play a complimentary role with other fire retardants. Among them, rare earth oxides have not had much attention for fire retardant purposes [5,6] and cerium (IV) oxide (CeO_2, ceria) has not been often investigated. Generally, ceria is considered a catalyst [7]. Jiao and Chen found that CeO_2 can have a synergistic effect when combined with aluminum hydroxide (ATH) in EVA/ATH/CeO_2 blends [8]. Sun et al. studied the fire retardancy and thermal degradation of wool treated with three rare earth oxide sols, including ceria [9]. There have been no reports using CeO_2 alone in fire retardancy in polymer matrices. The challenge of using metal oxides in a polymer matrix is the difficulty to obtain particles well-dispersed at the nano-scale, since metal oxides tend to agglomerate. Ceria has been reported to incorporate into poly (methyl methacrylate) (PMMA) using a sonochemical technique [10]. In this method, instead of employing ceria directly, a ceria precursor was combined with a small quantity of PMMA using a high intensity ultrasonic horn. Uniform distribution of ceria in the PMMA matrix was claimed. Pati et al. precipitated the precursor of CeO_2 using triethanolamine at room temperature [11]; this is a facile preparation of the ceria precursor.

Thus in this study, the precursor of CeO_2 was incorporated into PMMA and polystyrene (PS) by emulsion polymerization at two different loadings – during the synthesis the precursor hydrolyzes to CeO_2 – and the fire retardancy of the nanocomposites was studied. PMMA and PS were chosen to evaluate both a polar and a non-polar polymer with ceria.

2. Experimental

2.1. Materials

Cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99%), triethanolamine ($(C_2H_4OH)_3N$, 98%) anhydrous ethanol (≥99.5%), potassium persulfate (≥99%), sodium dodecyl sulfate (SDS, ≥99.0%) and methyl methacrylate (MMA, ≥98.5%) were acquired from Sigma–Aldrich and styrene was from J.T. Baker.

2.2. Preparation of CeO_2 precursor

The preparation of the CeO_2 precursor is similar to that described by Pati et al. [11]. A 100 mL portion of 1 mol/L cerium nitrate solution in anhydrous ethanol was placed in a 300 mL round bottom flask, and then with vigorous stirring, excess

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triethanolamine (90 g, 0.6 mol) was added at one time. The stirring was continued for 1 h after the completion of precipitation, and the solution was filtered. The precipitate was washed with anhydrous alcohol three times before drying at room temperature for 24 h. The resultant powder was then washed with acetone to remove the remaining alcohol, unreacted triethanolamine, and other byproducts. The precipitate, a precursor of CeO_2, is believed to be a cerium triethanolamine complex [11].

2.3. Emulsion polymerization of PMMA/CeO_2 and PS/CeO_2 nanocomposites

PMMA: a 6 g or 12 g portion of the as-prepared precursor was placed in 400 g distilled water in a 1000 mL three-neck round bottom flask with stirring, then 120 g MMA monomer was charged to the flask at one time. The flask was heated slowly to 50 °C to promote hydrolysis of the precursor, and then a 1.2 g portion of potassium persulfate, dissolved in 20 mL of distilled water, was added to initiate the polymerization under nitrogen protection. Since the hydrolysis of this precursor can produce triethanolamine, which is an emulsifier, additional emulsifier is not needed in the subsequent emulsion polymerization. The flask was maintained at 50 °C for 3 h. After cooling, the composite was filtered and dried in a vacuum oven at 80 °C overnight. Then the dried composite was broken into pieces and washed with distilled water 3 times to remove the inorganics in the composite. After filtering, the composite was dried in a vacuum oven at 80 °C for 24 h.

PS: the emulsion polymerization of PS/CeO_2 composite was not successful unless additional emulsifier was added and a higher temperature and longer time of reaction were used. The synthetic scheme for PMMA/CeO_2 was followed with a few changes: 1.2 g SDS was introduced as an additional emulsifier directly into the flask at the beginning, the temperature was increased to 75 °C and the reaction time was 6 h.

In order to confirm that CeO_2 is produced, the precursor was also hydrolyzed following the same procedure without polymer. According to calculation from the precursor, the low loading contains 2.3 wt% CeO_2 while the higher loading is 4.6 wt% CeO_2.

3. Instrumentation

A Rigaku Miniflex II desktop X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å) at a generator voltage of 30 kV and a current of 15 mA was used to study the diffraction behavior of pristine polymers and polymer/CeO_2 nanocomposites. All tests were conducted in the reflection mode at ambient temperature with 2θ varying between 2° and 45°. The scanning speed was 2°/min and the step size was 0.05°.

TEM images were obtained using a JEOL JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. The nanocomposite specimens were cut at room temperature using an ultramicrotome (Model MT-6000, Du Pont) with a diamond knife from an epoxy block where the films of the composites were embedded.

Thermogravimetric analysis (TGA) was conducted on a TA instruments SDT Q600 from room temperature (~25 °C) to 700 °C at a rate of 10 °C/min in a nitrogen atmosphere. The nitrogen flow rate is 100 mL/min. Samples were run in duplicate and the average values are reported; temperature is reproducible to ± 2 °C and mass to ± 0.2%.

The samples were investigated by TGA/FTIR using a Netzsch TG 209 F1 Iris coupled with a Bruker Tensor 27 FTIR to study the thermal degradation. The analyses were performed under flowing nitrogen at 20 mL/min. The TG resolution is 0.1 μg. The sample size was around 5 mg and the heating rate was 10 °C/min from room temperature to 700 °C. The coupling system between TG and FTIR was maintained at 200 °C to prevent condensation of evolved gases.

Pyrolysis combustion flow calorimetry experiments were carried out on a Govmark MCC-2 microscale combustion calorimeter (MCC). Samples weighing around 5 mg were heated to 750 °C at a heating rate of 60 °C/min in a stream of nitrogen flowing at 80 mL/min. The combustor temperature was set at 900 °C and oxygen/nitrogen flow rate was set at 20/80 mL/mL. The reported data are averages of 3 measurements and the typical relative error for heat release capacity is ±10%.

Cone calorimetry was performed on an Atlas CONE-2 according to ASTM E 1354 at an incident flux of 35 kW/m^2 using a cone shaped heater; exhaust flow was set at 24 L/s and the spark was continuous until the sample ignited. All samples were burned in triplicate and the data are the average of three replicated tests. Cone samples (about 30 g) were prepared by compression molding into 100 mm × 100 mm × 3 mm square plaques. Typical results from cone calorimetry are reproducible to within ±10% [12].

X-ray Photoelectron Spectroscopy (XPS) spectra (Al Kα) were recorded on a PHI Quantera-II SXM (Ulvac-PHI, Inc.) at 25 W under a vacuum of 2.6×10^{-7} Pa. The pass energy is 280.00 eV and the step length is 1 eV with a takeoff angle at 45°.

4. Results and discussion

4.1. XRD analysis

XRD patterns are presented in Fig. 1. The multiple peaks of ceria precursor indicate the product is not a single compound. Pati et al. suggested that the as-prepared precursor is a mixture of $[Ce(TEA)_2(NO_3)](NO_3)_2$, $Ce(OH)_4$, and $CeO_2 \cdot nH_2O$. Regarding the PMMA series, a broad hump at 13.5° in both PMMA/CeO_2 nanocomposites is indicative of PMMA. The other peak at about 28.6° in both PMMA/ceria nanocomposites, which is also present in the hydrolyzed precursor, can be associated with the cubic phase of cerium (IV) dioxide [11]. Apparently, from XRD only, all that is present is a small amount of cubic CeO_2 in PMMA. Similar observations can be made for the PS system, except for a few minor peaks found in PS/ceria composites, which may be due to the incomplete hydrolysis of CeO_2 precursor.

4.2. TEM observation

Figs. 2 and 3 present TEM images of high and low magnifications of PMMA- and PS-CeO_2 nanocomposites, respectively. At low magnification, agglomeration of the particles is seen and, not surprisingly, the distribution of the material is better at low concentration; this is true for both PS and PMMA. At high magnification, except for PMMA/CeO_2-4.6%, there is good homogeneous dispersion of CeO_2 particles in the polymer matrices. The particle size at low loading is less than 10 nm, which is consistent with the previous report [10]. Some of the particles at high loading are slightly larger than 10 nm, which indicates agglomeration may occur during the hydrolysis. This is more evident in PMMA/CeO_2-4.6% sample (Fig. 2).

The combination of XRD and TEM suggests that there is a small amount of cubic ceria present in the polymer; this likely is due to the presence of cubic ceria in the precursor. At low magnification, the dispersion in the polymer matrices is not very good. It is likely that this cubic ceria is present in large enough quantities so that is what is imaged here. At high magnification, the well-dispersed ceria is seen. The interpretation in this paper is that the cubic ceria phase that is seen in the XRD is what is imaged in the low magnification image; this cubic ceriais not well-dispersed in the polymers. On the other hand, there are also some well-dispersed fillers, which