Polymer Degradation and Stability 97 (2012) 2481–2486

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Polystyrene/molybdenum disulfide and poly(methyl methacrylate)/molybdenum disulfide nanocomposites with enhanced thermal stability

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ARTICLE INFO

Article history:
Received 28 July 2011
Received in revised form
4 January 2012
Accepted 4 January 2012
Available online 15 July 2012

Keywords:
Fire retardancy
Polystyrene
Poly(methyl methacrylate)
Nanocomposites

ABSTRACT

Nano-sized MoS_2 particles have been synthesized and polystyrene (PS) and poly(methyl methacrylate) (PMMA) nanocomposites have been prepared using solution mixing techniques. X-ray diffraction and transmission electron microscopy were used to characterize the morphology of the nanocomposites. Thermal stability and fire properties of nanocomposites were studied by thermogravimetric analysis and cone calorimetry. Mechanical properties were investigated by dynamical mechanical analysis and tensile testing. The PS/MoS_2 nanocomposites showed enhanced thermal stability in comparison to neat polystyrene, as exhibited by the increase of temperature of 50% mass loss point by over 30 °C in the best case. Reduction in the peak heat release rate was observed in all PS/MoS_2 nanocomposites and even more pronounced effects were found in PMMA/MoS_2 nanocomposite.

1. Introduction

Transition metal sulfides, especially molybdenum sulfide (MoS_2), are scientifically and technologically important materials. In recent years, their synthesis attracted ever increasing interest because of their potential applications in the areas of catalysis [1,2], lubrication [3–5], electrochemistry [6,7] as well as in intercalation chemistry where they serve as host materials [8,9]. Intercalation chemistry of metal sulfides was well known already in the 1970s but molybdenum disulfide has attracted scientific interest only in the last two decades.

MoS_2 exists in two crystalline forms, hexagonal and rhombohedral. The hexagonal form is by far the most common, found in commercial ores, but the rhombohedral form has also been found to occur in nature. The hexagonal form is characterized by MoS_2 layers in which the Mo atoms have trigonal prismatic coordination of six sulfur atoms, with two molecules per unit cell. This forms a layered structure consisting of MoS_2 sandwiches held together by relatively weak van der Waals forces. Each MoS_2 sandwich layer is composed of one molybdenum sheet between two sheets of sulfur and the atoms in a sheets form two-dimensional triangular net. The separation between the Mo sheet and S sheet is 1.59 Å and the distance between the Mo sheets of adjacent sandwich layers is 6.15 Å.

The literature reports several investigations in which MoS_2 has been combined with polymers and these studies have been carried out to increase toughness [10], to change the crystallization behavior in poly(phenylene sulfide) [11], for improved tribological properties [12,13] and to improve the thermal stability of i-polypropylene [14].

Over a period of several years, in this laboratory there have been investigations of the effect of a variety of nano-dimensional particles, including montmorillonite, layered double hydroxides and carbon nanotubes, on the fire retardancy of various polymers [15]. In this work, this is now extended to include MoS_2 as a nano-dimensional material.

In this work, dispersible MoS_2 nanoparticles were synthesized by the scale up of a literature procedure [16] using a mixture of the coordinating solvent trioctylphosphine oxide (TOPO) and octadecene as the synthetic medium. PS/MoS_2 and PMMA/MoS_2 nanocomposites were prepared and the thermal and fire properties of the nanocomposites with various amounts of molybdenum disulfide as a filler were investigated.

2. Experimental

2.1. Materials

Trioctylphosphine oxide (TOPO) technical grade, 90%; molybdenum hexacarbonyl ($Mo(CO)_6$), 98%; elemental sulfur (S); 1-octadecene (ODE), technical grade 90%; toluene, ACS reagent 99.5%; methanol, ACS reagent 99.9%; polystyrene (PS), nominal M_w

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http://dx.doi.org/10.1016/j.polymdegradstab.2012.07.004

192,000; poly(methyl methacrylate) (PMMA), nominal M_w 996,000; and dichloromethane, ACS 99.5%, were used as obtained from Aldrich Chemical.

2.2. Preparation of MoS_2 nanoparticles

MoS_2 nanoparticles were synthesized via reaction of $Mo(CO)_6$ with elemental sulfur in trioctylphosphine oxide at 270 °C using standard air-free techniques [16].

250 g of trioctylphosphine oxide and 15.0 g (56.8 mmol) of molybdenum hexacarbonyl were added to a 1000 ml three necked round bottom flask fitted with a flow control adaptor, a stopper and an air condenser. The system was brought into inert atmosphere by alternatively applying vacuum and flushing with argon three times. Reaction temperature was then increased to 250 °C under an argon atmosphere and the system was maintained at that temperature for 16 h.

The sulfur precursor solution was prepared by dissolving 3.64 g (113 mmol) of elemental sulfur in 75 ml of 1-octadecene at 130 °C under an Ar atmosphere. When a clear solution was obtained, the system was cooled to 60 °C. Then, the temperature of molybdenum-TOPO solution was increased to 270 °C and sulfur solution (maintained at 60 °C) was added drop-wise with a pipette in batches of 5 ml while maintaining the Ar atmosphere in both flasks. After the addition was complete, the reaction temperature was maintained at 270 °C for 48 h to complete the nanoparticle synthesis. The reaction system was then cooled to 60 °C and 60 ml of toluene was injected to the system to prevent solidification of reaction mixture. The dispersion was subsequently cooled to room temperature. The MoS_2 nanoparticles were isolated by adding an excess of methanol (1.5 l) followed by centrifugation; particles were purified by washing with methanol to remove the excess TOPO and then dried in an oven at 70 °C for 16 h. Yield: 12 g (since MoS_2 retains an unknown amount of TOPO, one cannot calculate the % yield).

2.3. Synthesis of PS/MoS_2 and PMMA/MoS_2 nanocomposites

PS/MoS_2 nanocomposites with 1, 5 and 10% of MoS_2 nanoparticles were prepared as follows. First, polystyrene (90 g) was dissolved in dichloromethane (600 ml) using a magnetic stirrer and ultrasonic agitation. Then, a previously prepared stable dispersion of MoS_2 nanoparticles (10 g) in dichloromethane (100 ml), was added to the PS solution and the system was mixed at room temperature for 48 h covered with aluminum foil followed by 4 h of stirring without cover to remove most of the solvent. Then, the viscous PS/MoS_2 solution was transferred to a container and dried at room temperature until most of the solvent evaporated. The remains were finally transferred to a vacuum oven and left at 70 °C overnight.

PMMA/MoS_2 nanocomposite with 10% of MoS_2 loading was prepared using an analogous procedure.

2.4. Characterization

X-ray diffraction measurements (XRD) were performed on a Rigaku, Miniflex II desktop X-ray diffractometer. Data acquisition was performed using a scan speed of 5°/min, at a sampling width of 0.05° from 2° to 65° (2θ). Transmission electron microscopy (TEM) was performed on a JEOL 1200 EXII microscope, equipped with a Tietz F224 digital camera and operated at an accelerating voltage of 80 kV. Sections 50–150 nm thick of the nanocomposites were obtained with a Leica Ultracut UCT microtome, equipped with a diamond knife. The sections were observed under bright field TEM without any heavy metal staining, since there was enough contrast to distinguish the inorganic fillers from the polymer matrix. Thermogravimetric analysis (TGA) was performed on a Netzch TG 209 F1 instrument. Samples were heated from 30 to 700 °C at a scan rate of 10 K/min under inert nitrogen atmosphere at a flow rate of 20 ml/min. Cone calorimeter measurements were performed on an Atlas CONE-2 instrument according to ASTM E 1352 at an incident flux of 50 kW/m [2] using a cone shaped heater. The exhaust flow was set at 24 L/sec. The specimens for cone calorimetry were prepared by the compression molding of the sample (approximately 30 g) into 10 cm × 10 cm square plaques with thickness of 3 mm. Dynamical mechanical analysis (DMA) was performed on a DMA-Q800 TA instrument in air between 30 and 120 °C with heating rate of 3 °C/min. The tensile test was performed on an Instron 5500 series test instrument at room temperature. The crosshead speed was 12.7 mm/min. Specimens for tensile test were prepared with a CS-183MMX Mini Max molder injection machine.

3. Results and discussion

Fig. 1 shows the X-Ray diffraction (XRD) patterns of commercial MoS_2 and the synthesized MoS_2 nanoparticles. It appears that the commercial MoS_2 has strong crystallinity and a layered structure with an interlamellar distance of 6.15 Å (0.615 nm), as seen from the high order diffraction peaks (004), (006) and (008) shown in Fig. 1. This highly crystalline [17] material is very difficult to exfoliate and disperse in polymer matrices without special procedures [18–20]. However, MoS_2, synthesized by the method described above is unambiguously amorphous as shown by the lack of crystalline or high-order basal peaks in the XRD diffractograms and is therefore presumably very dispersible in various polymer matrices. The absence of the (002) reflection at 6.15 Å ($2\theta = 14.5°$) and a broad feature indicating the absence of crystalline long-range order, strongly suggests a large extent of destacking in the synthesized MoS_2. Fig. 2 shows the XRD pattern of PS/MoS_2 nanocomposite with 5% of MoS_2 as compared to the filler itself. The broad MoS_2 diffraction peak at $2\theta = 9.5°$ is still present in the PS nanocomposite, as a low-2θ shoulder in the PS amorphous halo. However, the broad MoS_2 basal peak at $2\theta = 32–38°$ is barely visible in the PS nanocomposite, suggesting some dispersion of the nanoparticles in the PS matrix. The same observations are observed for PMMA/MoS_2 nanocomposites but not shown here.

The composite morphology of the PS/MoS_2 nanocomposites was further studied by TEM analysis. Fig. 3 presents TEM images of PS/

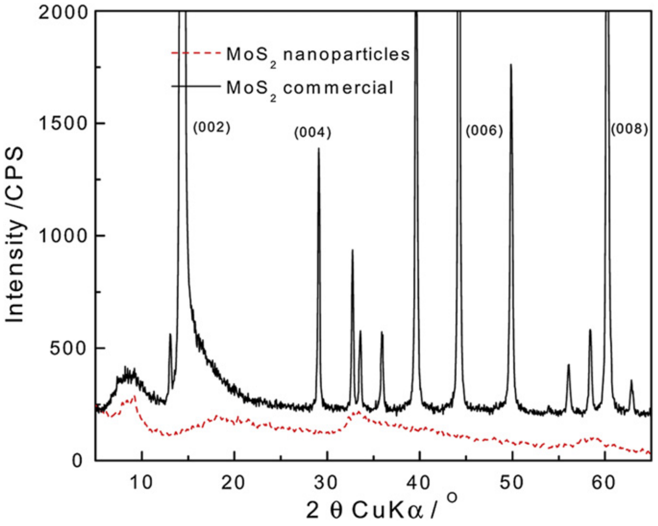

Fig. 1. XRD patterns of commercial MoS_2 and synthesized MoS_2 nanoparticles.