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ScienceDirect
Polymer Degradation and Stability 93 (2008) 77–83
Polymer Degradation and Stability
www.elsevier.com/locate/polydegstab

# Influence of α-$Fe_2O_3$ nanorods on the thermal stability of poly(methyl methacrylate) synthesized by *in situ* bulk polymerisation of methyl methacrylate

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Received 9 July 2007; received in revised form 16 October 2007; accepted 22 October 2007
Available online 30 October 2007

**Abstract**

α-$Fe_2O_3$ nanorods were incorporated into poly(methyl methacrylate) (PMMA) by *in situ* radical polymerisation of methyl methacrylate initiated by 2,2′-azobisisobutyronitrile. The α-$Fe_2O_3$ nanorods were synthesized by forced hydrolysis of $FeCl_3$ and structural characterization was performed by X-ray diffraction and transmission electron microscopy. The molar mass and the polydispersity index of synthesized PMMA samples were determined by gel permeation chromatography. The content of residual monomer was determined by $^1$H NMR spectroscopy. The influence of α-$Fe_2O_3$ nanorods on the thermal stability of the polymer was investigated using thermogravimetry and differential scanning calorimetry. The molar mass and polydispersity index of PMMA were dependent on the content of α-$Fe_2O_3$ nanorods. The values of the glass transition temperature of the nanocomposites were lower compared to pure PMMA. Also, the thermal stability of nanocomposites in nitrogen and air was different from that of pure PMMA.


*Keywords:* α-$Fe_2O_3$ nanorods; PMMA; Nanocomposite; Bulk radical polymerisation

## 1. Introduction

Incorporation of inorganic nanoparticles in a polymer matrix can significantly affect the thermal, mechanical, optical, electrical, magnetic and flammability properties [1,2]. Additionally, nanocomposites have many advantages, such as increased strength (without compromising other mechanical properties), improved heat resistance, decreased gas permeability, and enhanced electrical conductivity over traditional polymer composites prepared with fillers in the micrometer size domain. The properties of polymer nanocomposites depend on the type of incorporated nanoparticles, their size and shape, as well as the concentration and interaction with the polymer matrix [3–7].

Iron oxide nanoparticles are of special significance because of their application in catalysis, as gas sensors, magnetic storage, ferrofluids, magnetic refrigeration and colour imaging. The influence of ferric oxide nanoparticles on the thermal properties of polymer nanocomposites has been widely studied [8–15]. The influence of the shape of the nanoparticles on the thermal stability of the polymer matrix was investigated by incorporating β-FeOOH nanorods in a poly(methyl methacrylate) (PMMA) matrix [11]. A better thermal stability, with the same amount of inorganic phase, was achieved by β-FeOOH nanorods with a larger aspect ratio. The presence of $Fe_2O_3$ in a PMMA matrix improves the thermal stability and fire retardant properties of the polymer in a synergistic manner when mixed with organoclays, the most promising flame retardant additives [12,13].

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0141-3910/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2007.10.015

In the above-mentioned studies, the nanocomposites were obtained by dispersing the nanoparticles either in a polymer solution or in a polymer melt, using commercially available polymers. However, PMMA obtained in the shape of sheets by bulk polymerisation of methyl methacrylate (MMA) is used for many applications. Thus, in this study, PMMA/α-$Fe_2O_3$ nanocomposites were prepared by bulk radical polymerisation of MMA in the presence of α-$Fe_2O_3$ nanorods. The influence of α-$Fe_2O_3$ nanorods on the molar mass, polydispersity index (PDI), glass transition temperature ($T_g$) as well as on the thermal stability of the PMMA matrix in nitrogen and air was investigated using gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetry (TG). The structural characterization of α-$Fe_2O_3$ nanorods was performed by X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM).

## 2. Experimental

### 2.1. Materials

Ferric chloride ($FeCl_3$) was purchased from Aldrich, methyl methacrylate from Merck and 2,2′-azobisisobutyronitrile (AIBN) from Fluka. All chemicals were used as received without further purification. Commercially available PMMA Diakon CMG 314V ($M_w = 90{,}000$; $M_w/M_n = 2.195$) was purchased from Lucite International.

### 2.2. Preparation of α-$Fe_2O_3$ nanorods

A dispersion containing α-$Fe_2O_3$ nanorods was obtained by forced hydrolysis of an $FeCl_3$ solution in a manner similar to the method described in literature [16]. To 100 ml of 2 M $FeCl_3$ was added 100 ml of 5.4 M NaOH, and the solution was stirred at room temperature for 15 min. Subsequently, the solution was heated to 100 °C and the temperature was maintained for 8 days. The α-$Fe_2O_3$ nanorods were recovered by centrifugation, washed several times with water and dried in a vacuum oven.

### 2.3. Preparation of α-$Fe_2O_3$/PMMA nanocomposites

In order to prepare samples of PMMA/α-$Fe_2O_3$ nanocomposite by bulk polymerisation of MMA, the appropriate amount of α-$Fe_2O_3$ nanorods was added to 7.5 g of MMA and ultrasonically dispersed. Then, 1.5 g of PMMA (Diakon CMG 314V) was added and the dispersion was stirred using a magnetic stirrer at room temperature overnight. The dispersion was heated up to 50 °C and 13.5 mg of the initiator, AIBN, dissolved in 0.8 g MMA was introduced. The obtained dispersion was stirred using a magnetic stirrer at 50 °C for 20 min and then quickly poured between two parallel glass plates with a 1 mm Teflon spacer and polymerised at 60 °C for 4 h and subsequently at 120 °C for 1 h. The polymerisation of MMA without the presence of α-$Fe_2O_3$ nanorods was performed under the same experimental conditions.

### 2.4. Characterization

The X-ray diffraction (XRD) measurement of a solid phase of α-$Fe_2O_3$ dispersion was performed using a Philips PW 1710 diffractometer.

Microstructural characterization of the α-$Fe_2O_3$ nanorods was performed on a transmission electron microscope (TEM) Philips EM-400. The samples for microscopic analysis were deposited on C-coated Cu grids.

The molar masses and PDIs of the synthesized PMMA samples were determined using a Spectra-Physics chromatograph equipped with a differential refractive index detector and a set of two gel columns (MZGPC columns) with porosities of 1000 Å. Tetrahydrofuran, 1.0 ml/min, was used as the mobile phase. Narrow molar mass polystyrene standards (Polymer Standards Service) were used for the calibration. The molar mass characteristics of the examined samples were calculated using Chrom Gate 3.1.4. software (Knauer). For the GPC measurements, PMMA was extracted from the PMMA/α-$Fe_2O_3$ nanocomposite with acetone. Subsequently, PMMA was obtained by evaporation of acetone.

The $^1H$ NMR spectra of the synthesized samples were recorded in deuterated chloroform using a Bruker DRX 500 NMR spectrometer. Tetramethylsilane was used as the internal standard.

The thermal stability of PMMA and PMMA/α-$Fe_2O_3$ nanocomposites was investigated by non-isothermal thermogravimetry (TG) using a Perkin Elmer TGS-2 instrument. The measurements were conducted at a heating rate of 10 °C/min in a dynamic nitrogen atmosphere or air (flow rate 25 $cm^3$/min).

Differential scanning calorimetry (DSC) was performed at a heating rate of 20 °C/min in a nitrogen atmosphere using a Perkin Elmer DSC-2 instrument.

## 3. Results and discussion

The XRD pattern of the solid phase of the synthesized dispersion is shown in Fig. 1. The XRD peaks exactly matched

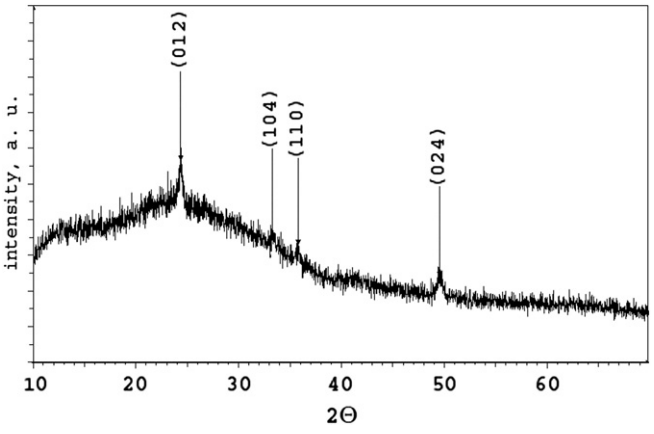


Fig. 1. The XRD pattern of the α-$Fe_2O_3$ nanorods.