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Influence of TiO_2 and Fe_2O_3 fillers on the thermal properties of poly(methyl methacrylate) (PMMA)

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Abstract

The thermal properties of pure poly(methyl methacrylate) (PMMA) and PMMA filled with 5%, 10%, 15% and 20% of nanometric particles of titanium oxide (TiO_2) and ferric oxide (Fe_2O_3) were investigated under air atmosphere by DSC, TGA and LOI measurements on samples prepared by solvent casting method. In the presence of the filler, the thermal stability of the polymer appeared to be significantly improved. A linear relationship between LOI and glass transition temperature (T_g) suggests that the restriction of mobility of the polymer chains is directly linked to the increase of stability.
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1. Introduction

The improvement of thermal and flammability properties of polymer materials is a major concern, particularly in the domains of transportation, building, civil and electrical engineering. Numerous and recent studies have shown the interest of the use of lamellar nanofillers (above all modified montmorillonites) as flame retardants [1,2] or as components of flame retardants systems [2]. Moreover, the use of oxide particles in the submicronic or nanometric range as synergistic agents in addition to usual fire retardant additives seems to be very promising. Since a few years ago, we are involved in the search of strongly fire retarded poly(methyl methacrylate) (PMMA), and, at present, we have undertaken researches with such an approach. In a first step, we are investigating the influence of oxide fillers alone on the thermal properties of PMMA before to incorporate them as synergistic agents of phosphorous flame retardants. This paper presents the first results obtained with Fe_2O_3 and TiO_2 fillers.

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2. Experiments and results

2.1. Sample preparation

The poly(methyl methacrylate) was from Aldrich with a weight-average molecular weight of 350,000 g mol^{-1} (based on GPC analysis) and obtained by free radical synthesis.

Commercial TiO_2 from Degussa (P-25 99.5%) with a mean particle size of 21 nm was used. The surface area was checked by the BET method and found equal to 48 m^2 g^{-1}. Submicron Fe_2O_3 particles were prepared according to the procedure described by Deb et al. [3]. The method is based on the precipitation of ferric oxide hydroxide (FeOOH) from a ferric nitrate solution, followed by heat treatment to completely decompose the organic layer and FeOOH into Fe_2O_3. X-ray diffraction analysis after heat treatment at 400 °C showed the co-existence of α- and γ-Fe_2O_3 (Fig. 1) even if the samples were treated during a few hours. However, heat treatment at 500 °C during 2 h resulted in only the α phase (Fig. 1). The surface area was measured by BET and was equal to 52 m^2 g^{-1}. Under the scanning electron microscope, the iron oxide powder appeared in the form of

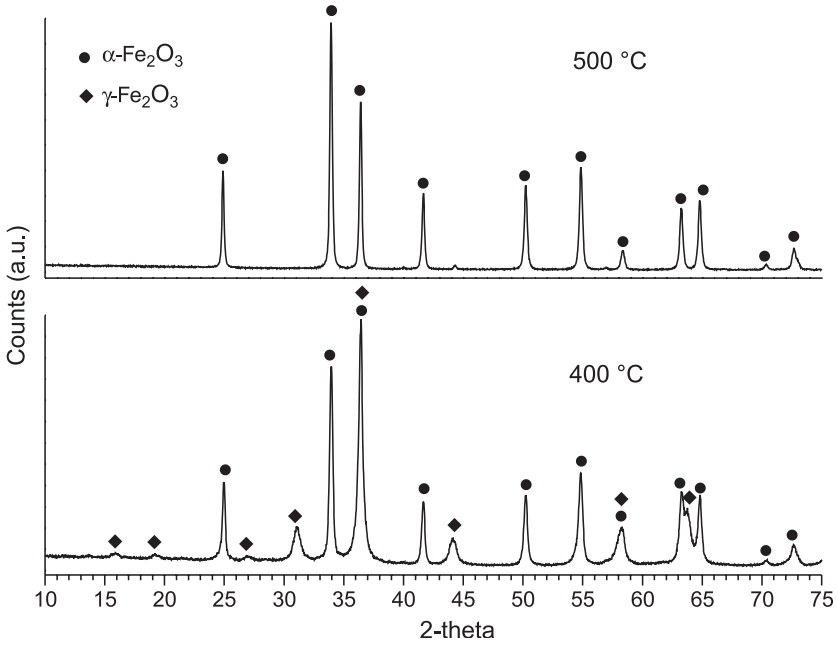

Fig. 1. X-ray powder diffraction patterns of the synthesized Fe_2O_3 after heat treatment at 400 and 500 °C.

agglomerates (Fig. 2), whereas transmission electron microscopy showed that these agglomerates were formed from plate-like particles (estimated minimum size: (100–200)×(7–10)nm).

The PMMA/oxide-filled polymer samples were prepared by dissolving PMMA into chloroform (typically 1 g for 50 cm^3). The solution was stirred at 50 °C during 30 min. Then, the appropriate amount of TiO_2 or Fe_2O_3 was added and ultrasonically dispersed during a few hours at room temperature in order to obtain a good dispersion of the oxide particles into the polymer matrix. Afterwards, the samples were dried during 4 h to complete the evaporation of chloroform. Treatment at about 70–80 °C as commonly performed in the literature was found to be quite non-effective as shown by TGA experiments where an unexpected weight loss was recorded at about 170 °C which was found to correspond to chloroform volatilization by Py-GC-MS analysis. The temperature of 170 °C was then checked to provide samples free of chloroform.

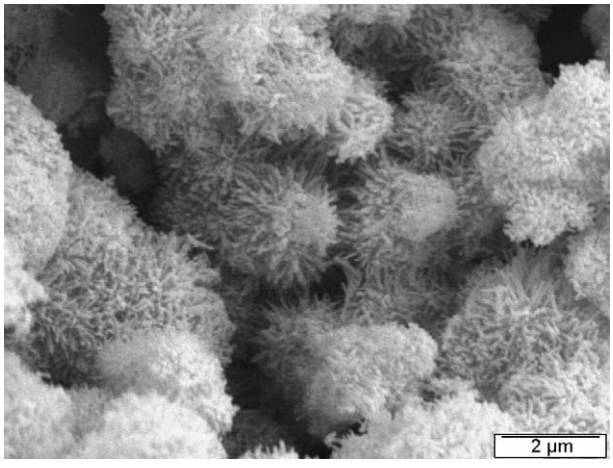

Fig. 2. Typical SEM micrographs of the Fe_2O_3 powder after heat treatment at 500 °C.

2.2. Experimental techniques

Glass transition temperatures (T_g) were measured within 0.5 °C with a Setaram DSC-92 apparatus with an heating rate of 10 °C min^{-1}. The samples (20–25 mg) were placed into aluminum crucibles.

Thermogravimetric studies were performed with a Mettler-Toledo TGA/SDTA 851e apparatus operating in air atmosphere. The runs were carried out in dynamic conditions at 10 °C min^{-1} between 30 and 600 °C. Alumina crucibles were used and the sample weight was about 20–25 mg.

The limiting oxygen index (LOI), defined as the minimum oxygen amount, in an oxygen–nitrogen flow, required to completely burn down the material during at least 30 s [4] was determined with an apparatus described in NFT 51-07 using a modified procedure [5]: Pellets of the sample (200 mg) were placed on an aluminum sample holder (height: 25 mm, length: 55 mm, width: 18 mm) located in the middle of the chimney (diameter: 80 mm, height: 540 mm). The values never represented the absolute LOI (ASTM D 2863-77) of the samples but were found to be quite reproducible compared to those obtained for six usual polymers [6]. The oxygen amount was measured with a thermal flow meter Calibrage DGM (mass flow meter Brooks 5850 TR at room temperature, in-pressure: 2 bar and out-pressure: atmosphere). The measurements were performed with an oxygen amount step equal to 0.5.

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