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The catalytic role of oxide in the thermooxidative degradation of poly(methyl methacrylate)–TiO_2 nanocomposites

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ABSTRACT

The influence of TiO_2 nanoparticles on the thermal degradation of poly(methyl methacrylate) (PMMA) was investigated by TGA. The studied materials were characterized by Py–GC–MS, TEM, SEM, TGA, DSC and TGA–MS. The PMMA–TiO_2 nanocomposites were prepared by melt blending with different (5, 10, 15 and 20 wt% TiO_2) loadings. According to TGA results and to the activation energy (determined by the model-free isoconversional method of Vyazovkin), the incorporation of 5 wt% of TiO_2 nanoparticles into PMMA stabilizes it by more than 40 °C. However, for higher loading contents, a catalytic effect on the thermal decomposition was observed which increased with the oxide content. The results obtained by Py–GC–MS showed clearly that TiO_2 increases the formation of methanol, methacrylic acid and propanoic acid methyl ester during the degradation of PMMA. This catalytic effect could be explained through the interaction of the methoxy group of the methacrylate function with the hydroxyl groups present at the surface of the oxide particles.

1. Introduction

In recent years, the potential of using metal oxides as fillers in polymers has become appreciated in several applications. The composite obtained might exhibit improved thermal, electrical, mechanical, optical and fire resistance properties. However, to gain a better knowledge of the influence of these fillers on the thermal degradation of the polymer still needs further studies. Among the papers published about this subject, it appears that the majority of the work performed particularly concerns poly(methyl methacrylate) filled with silica particles.

Kashiwagi et al. [2] studied the influence of silica specific surface area on the thermal stability of PMMA. With a loading of 10 wt%, no remarkable change in the thermal stability of PMMA was observed, despite the use of silica with a very high specific surface area ($400\ m^2\ g^{-1}$). In another work, also carried out by Kashiwagi et al. [3], silica nanoparticles (12 nm) were used to prepare PMMA–SiO_2 nanocomposite by in situ polymerization. In this case, only a little improvement in the thermal stability was observed.

To explain the improvement observed for the thermal stability of PMMA–SiO_2 nanocomposites, Feng and Gordon [4] invoked the restriction of mobility of polymer chains resulting from the steric hindrance due to the presence of the filler. However, Hu et al. [5] attributed the increase of the thermal stability of PMMA–nanosilica composites to the high silica specific surface area and perhaps to the ability of silica particles to trap radicals during polymer degradation. On the other hand, the observed increase of the glass transition temperature of this system was explained by the restriction of mobility of polymer chains.

Aruchamy et al. [6] reported that the enhancement of the thermal stability of PMMA–silica composites was due to a hydrogen-bonding interaction between carbonyl groups in PMMA and hydroxyl groups of the silica surface. The hydrogen bonds could interrupt the depolymerisation of the polymer chains. Thus, the increase of interaction sites on the surface could lead to on increase of the temperature of decomposition. However, this hypothesis was rejected by Hu et al. [5] reporting that although the thermal stability of PMMA was increased, no OH groups were present on the surface of modified silica particles. The improvement of thermal stability was then explained by a trapping effect of the radicals by the silica particles which also acted as a gas barrier preventing the degradation products from diffusing out the composite. Morgan et al. [7] also observed a higher decomposition temperature for PMMA–SiO_2 nanocomposite than pure PMMA which was also attributed to the gas barrier function of silica particles.

We performed some previous studies about the influence of Fe_2O_3 and TiO_2 nanoparticles on the thermal stability of PMMA. It was proposed that the improvement of the thermal stability was

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the result of two main factors: (i) restriction of mobility of the polymer chains caused by the steric hindrance due to the presence of particles and (ii) bonds due to the adsorption of polymer on the oxide surface via methoxycarbonyl groups (–C(O)OCH$_3$) [8,9]. Accordingly, it was also proposed that the adsorption phenomena could modify a key step of the reaction mechanism involved.

The aim of the present work was to study the effect of the amount of TiO$_2$ nanoparticles on the degradation mechanism of PMMA in order to confirm the preceding interpretations. For this purpose, the reaction mechanism and kinetics were investigated via a model-free method and the identification of key degradation products.

2. Experimental

2.1. Materials

The poly(methyl methacrylate) (Oroglas, Mw = 93 000 g mol^{-1}) was supplied by Arkema. Nanometric titanium oxide (TiO$_2$) was produced by Degussa (median particle size: 21 nm, BET specific surface area: 50 m^2 g^{-1}). Micrometric titanium oxide was produced by Panreac (median particle size:0.2 μm, BET specific surface area: 5.8 m^2 g^{-1}).

2.2. Preparation of nanocomposites

All composites were prepared by mixing, in an appropriate ratio, the molten PMMA pellets and the filler~~s~~ (TiO$_2$) in a Haake PolyLab 60 cm^3 mixer rheometer at 225 °C and 50 rpm. Total mixing time was typically 7 min. Resulting composites were then pelletized using a rotary cutter mill before being moulded by compression at 250 °C and 100 bar for 5 min. The contents of inorganic phase were chosen to be 0, 5, 10, 15 and 20 wt%.

2.3. TEM and SEM

Scanning electron microscopy (SEM) micrographs of PMMA–TiO$_2$ nanocomposites were made using an environmental microscope (FEI-Quanta 200 type). TEM observations were performed with a Hitachi H800 MT at 200 kV.

2.4. Thermogravimetric analysis

The thermal degradation behaviour was studied by thermogravimetric analysis (TGA). The TGA apparatus was a Mettler-Toledo TGA/SDTA 851e thermobalance (horizontal balance mechanism), operating in air environment under a gas flow of 65 cm^3 min^{-1} with alumina crucibles (70 μl) containing 5–6 mg of sample. The runs were carried out in dynamic conditions at the constant heating rates of 2, 5, 10 and 20 °C min^{-1}. Two TGA experiments' runs were performed for each sample. The repeatability of TGA measurements was confirmed with preliminary investigations on the thermal degradation of virgin PMMA for which duplicate measurements were performed at different heating rates. The uncertainties on temperature and mass measurements were, respectively, estimated to be 0.5 °C and 0.1 mg.

TGA–MS was performed under air flow (100 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1} from 30 to 600 °C with a Netzsch-STA 409 PC apparatus coupled with a mass spectrometer Netsch-Aeolos 403C.

2.5. DSC

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) using a Netzsch 204 F1 equipment. Measurements were performed in the temperature range 25–200 °C under a nitrogen flow and with a heating rate of 10 °C min^{-1}. About 15 mg of samples were heated from 25 to 200 °C, held at this temperature for 5 min, cooled to 25 °C, held for 5 min, and then heated again to 200 °C. The values of glass transition temperature were taken as the midpoint of the glass transition event. The uncertainty on temperature was estimated equal to 0.5 °C.

2.6. Py–GC–MS

The Py–GC–MS experiments were performed with a CDS Pyroprobe 2000 coupled with a HP Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column (crosslinked 5% PH-ME siloxane, 30 m length, 0.25 mm diameter, 0.25 μm film thickness). The GC oven was set to 35 °C for the first 5 min, then heated with a rate of 10 °C min^{-1} up to 250 °C and held for 40 min. The GC was connected to a mass selective detector (HP Agilent 5973) operating in the electron impact mode at 70 eV energy. The source and quadrupole were, respectively, held at 230 and 250 °C. The mass scanning range was 10–750 uma. The carrier gas used was helium at constant flow (1.1 ml min^{-1}). Initial sample weight was set at about 1 mg for each experiment. Flash pyrolysis was used during 60 s from 25 to 400 °C (heating rate: 5000 °C s^{-1}).

3. Experimental results

3.1. Morphology of composites

The TEM analysis of the PMMA–5TiO$_2$ nanocomposite (PMMA loaded with 5 wt% TiO$_2$) was performed in order to investigate the dispersion and distribution of nanoparticles of TiO$_2$ in the matrix. Fig. 1 shows a typical micrograph obtained. It can be observed that the oxide nanoparticles are well distributed in the material but with some tendencies to aggregation. The size of the aggregates is much smaller than 0.2 μm, and very rarely it could be found aggregates in the micrometric range. The tendency to aggregation can be explained by the fact that no surface treatment was performed on the oxide particles. Fig. 2 shows the SEM micrographs of the polished surface of the composites with different TiO$_2$

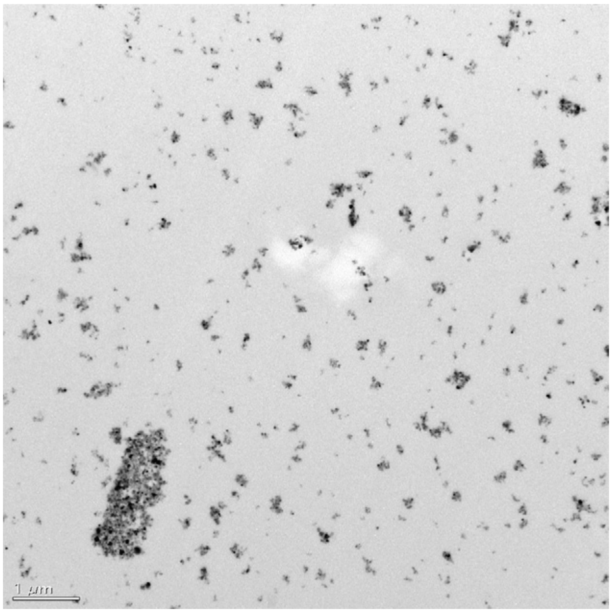

Fig. 1. TEM image of PMMA–5TiO$_2$ nanocomposite.