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Synthesis and characterization of NiO nanoparticles and their PMMA nanocomposites obtained by in situ bulk polymerization

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Abstract A nickel oxide (NiO) precursor was prepared using Pechini method. The NiO nanoparticles were prepared by calcination of NiO precursor at temperatures ranging from 300 to 700 °C. The resulting NiO nanoparticles were characterized by X-ray photoelectron spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy. To hamper NiO nanoparticles aggregation, the NiO nanoparticles surface was treated using (3-mercaptopropyl)-trimethoxysilane as a coupling agent. Next, nanocomposites of poly(methyl methacrylate) and modified NiO nanoparticles were successfully prepared by in situ bulk polymerization with 2,2′-azobis(isobutylonitrile) as initiator. The obtained nanocomposites were characterized by XRD and thermogravimetric analysis.

Introduction

Polymeric nanocomposites are a new class of materials that combine the properties of inorganic particles with the processability and flexibility of an organic polymer matrix. The resulting hybrid materials offer the possibility of a new generation of nanostructured materials with diverse applications such electronic or photonic devices, sensors, and catalysts [1–3].

There are a broad variety of available polymers that can be used to prepare nanocomposites. The poly(methyl methacrylate) (PMMA) has been one of the most widely studied in the last decade due to its promising mechanical and chemico-physical properties. PMMA is an important member of the polyacrylic and methacrylic esters family. PMMA has several desirable properties, including exceptional optical transparency, good mechanical properties, good weatherability, acceptable thermal stability, desirable electrical properties, moldability, and easy shaping [4]. Similarly, nickel oxide (NiO) has been under extensive investigations for the last years as an important inorganic material in several applications. It has been reported in batteries, electrochromic material, catalysts, electrodes, gas sensor, and in the electronic industry [5–10]. Polymer/NiO nanocomposites in different polymer matrices have been prepared for applications as magnetic materials [11], gas sensors [12], and light-emitting and electronic devices [13].

In this work, NiO nanoparticles are synthesized by the Pechini method. The obtained nanoparticles were treated with a silane coupling agent and then used to prepare PMMA/NiO nanocomposites by in situ bulk polymerization. The structural and morphological properties of the NiO nanoparticles were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The thermal properties of the PMMA/NiO nanocomposites were evaluated by thermogravimetric analysis (TGA).

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Experimental details

The starting chemicals used in this work were citric acid (CA), ethylene glycol (EG), nickel acetate, (3-mercaptopropyl)-trimethoxysilane (MPTMS), and methyl methacrylate (MMA) of reagent grade (>98%) purchased from Aldrich. 2,2′-azobis(isobutyronitrile) (AIBN) (initiator) was recrystallized with ethanol.

The NiO nanoparticles were prepared by Pechini method [14] as follows. First, the appropriate amounts of CA and EG were mixed and stirred at room temperature until a transparent solution is obtained. Then, nickel acetate was added and the mixture was further stirred to achieve complete solubility. The resulting solution was heated at 130 °C for 48 h in order to obtain the precursor material. After that, we obtained a green solid mass, which was ground using a planetary mill. The obtained powder was calcined between 300 and 700 °C for 2 h in air.

Nickel oxide functionalization was performed as follows. A specific amount of NiO nanoparticles were mixed with 35 mL of octane, and then MPTMS was added to the system. The proportion of NiO and MPTMS was kept at 1:1. The mixture was heated (reflux) for 6 h. At the end of the reaction, the mixture was cooled down and decanted. The NiO-treated nanoparticles were dried at 40 °C in vacuum for 24 h.

Poly(methyl methacrylate)–NiO nanocomposites with three different concentrations of 0.1, 0.25, and 0.5 wt% of NiO nanoparticles were prepared by in situ bulk polymerization method as follows. Different amounts of modified NiO nanoparticles and 5 ml of MMA were mixed in glass tubes. The weight fraction of NiO was adjusted with respect to MMA. The mixtures were sonicated for 15 min before the polymerization. After that, AIBN (0.1 wt%) was added and four cycles of a freeze–thaw process were applied prior to polymerization. The glass tubes were sealed at vacuum and placed into a preheated silicone oil bath at 70 °C and stirrer with a magnetic stirrer for 5 h at that temperature.

X-ray diffraction measurements were performed with a Siemens D5000 diffractometer using a Cu Kα radiation source. The size and morphology of the NiO nanoparticles were determined by TEM using a JEOL 2010 HRTEM. Thermogravimetric analysis (TA instrument TGA Q500) was carried out with a heating/cooling rate of 10 °C min^{-1} under nitrogen. XPS data were acquired with Al Kα radiation using a fixed analyzer. The binding energy values were referenced to the C1s level (284.5 eV).

Results and discussion

The XRD patterns of the NiO nanoparticles obtained at different temperatures are shown in Fig. 1. The XRD pattern of the sample obtained at 300 °C clearly shows the characteristics peaks of cubic NiO [15] located at 37.3°, 43.3°, 62.9°, 75.4°, and 79.4°. Also, some peaks located at 44.5°, 51.8°, and 76.3° corresponding to fcc metallic nickel [16] as second phase were observed. For the sample obtained at 500 °C, small peaks of Ni phase are observed, when the temperature of the calcination increases at 600 and 700 °C, only the NiO phase is presented. Since we know that an increase in calcinations temperature results in an increase in crystallite size, leading to sharper diffraction peaks; we selected the nanoparticles obtained at 600 °C to prepare the nanocomposite. Also, this temperature shows only NiO phase.

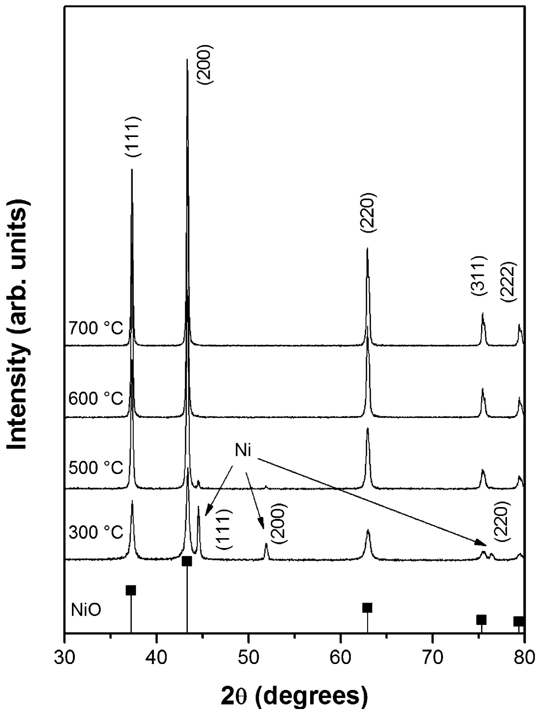

Fig. 1 XRD patterns of NiO nanoparticles obtained at different temperatures

Figure 2 shows XPS spectra taken from the Ni (a) and O (b) regions of NiO nanoparticles and MPTMS-modified NiO nanoparticles. The data show that both Ni and NiO are present in the sample. The non-modified NiO nanoparticles shown in Fig. 2a show peaks at about 853.7 and 872.2 eV are attributed to $Ni2p_{3/2}$ and $Ni2p_{1/2}$ in NiO. The gap between the $Ni2p_{1/2}$ and $Ni2p_{3/2}$ level is 19 eV, consistent with the split orbit for Ni. The peaks at ~860 and 867 eV correspond to the $Ni2p_{3/2}$ and $Ni2p_{1/2}$ in metallic nickel. The spectra for the modified NiO nanoparticles shown in Fig. 2a shows similar features than those observed in the modified nanoparticles. The lower intensity is attributed to the surface functionalization of the NiO nanoparticles. The functionalizing film in the NiO nanoparticles lowers the number of photoelectron reaching the detector, resulting in lower intensity. In the O1s region (Fig. 2b), the non-treated

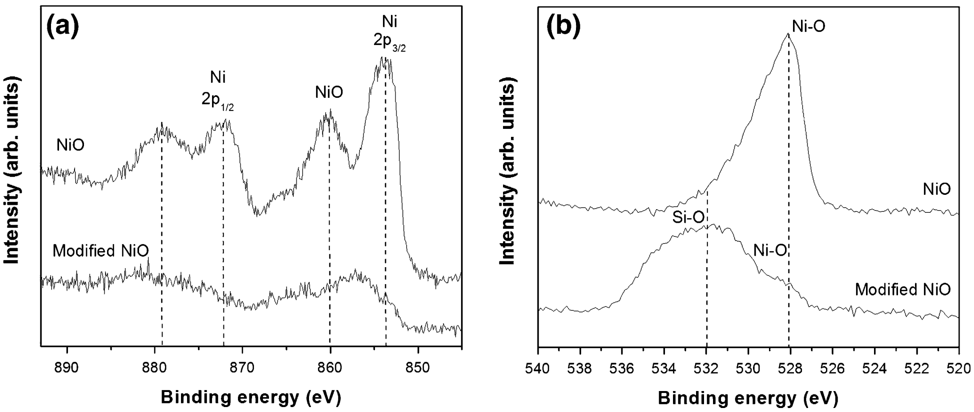

Fig. 2 XPS analysis of the NiO nanoparticles and modified-NiO nanoparticles. Ni region (**a**) and O region (**b**)

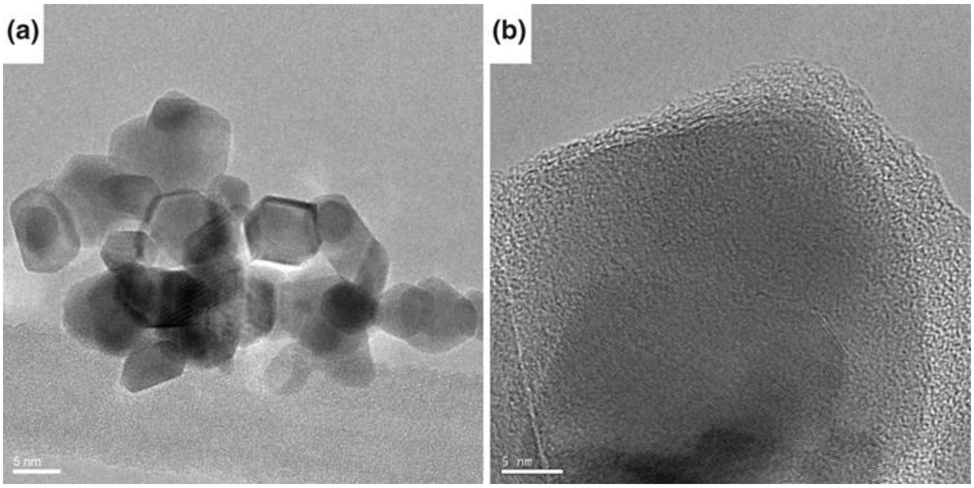

Fig. 3 TEM images of NiO nanoparticles (**a**) and modified-NiO nanoparticles (**b**)

NiO nanoparticles show the presence of mostly NiO. However, the modified NiO nanoparticles show the presence of both NiO and SiO, consistent with the Ni2p results and confirming the presence of a thin SiO-like film on the surface of the NiO particles.

Figure 3 shows the TEM images of the NiO nanoparticles obtained at 600 °C (a) and the MPTMS modified-NiO nanoparticles (b). From this image, it is clearly seen that the NiO nanoparticles are mostly irregularly shaped. The size of these particles has a distribution ranging from 10 to 30 nm. The modified NiO nanoparticles show an amorphous coating due to the MPTMS treatments, consistent with the XPS results discussed above.

Figure 4a shows the XRD patterns of PMMA and PMMA/NiO nanocomposites with different concentration of NiO nanoparticles. The XRD pattern of PMMA exhibits two amorphous halos, a large hump centered at $2\theta = 13°$ and a small hump at $2\theta = 30°$ [17]. In the PMMA/NiO nanocomposites, besides the amorphous halos, the characteristics peaks of NiO located at 37.3°, 43.3°, 62.9° can be also observed in the samples with 0.25 and 0.5 wt%.

The thermogravimetric curves of the PMMA and PMMA/NiO nanocomposites under air flow are shown in Fig. 4b. The figure shows that the PMMA/NiO nanocomposites have higher decomposition temperatures when compared to PMMA. As an example for 50% weight loss, the nanocomposite with 0.5 wt% NiO nanoparticles showed a 35 °C increase in decomposition temperature with respect to PMMA. The addition of the NiO nanoparticles improves the thermal properties of the nanocomposites obtained and it is related to the concentration of NiO nanoparticles. The extent of improvement of the thermal stability of PMMA upon incorporation of NiO nanoparticles is comparable to improvement achieved using other nanoparticles fillers such as ZnO [18, 19] and TiO_2 [20]. The possible mechanism of improvement the thermal stabilization is the interaction between the surface of the filler (NiO particles) and segments of the PMMA polymer chain, which reduces segmental mobility, as been reported in β-FeOOH/PMMA [21], graphite/PMMA [22], and CdS/PMMA [23] nanocomposites.

Conclusions

Poly(methyl methacrylate)/NiO nanocomposites were synthesized through in situ polymerization of MMA monomer

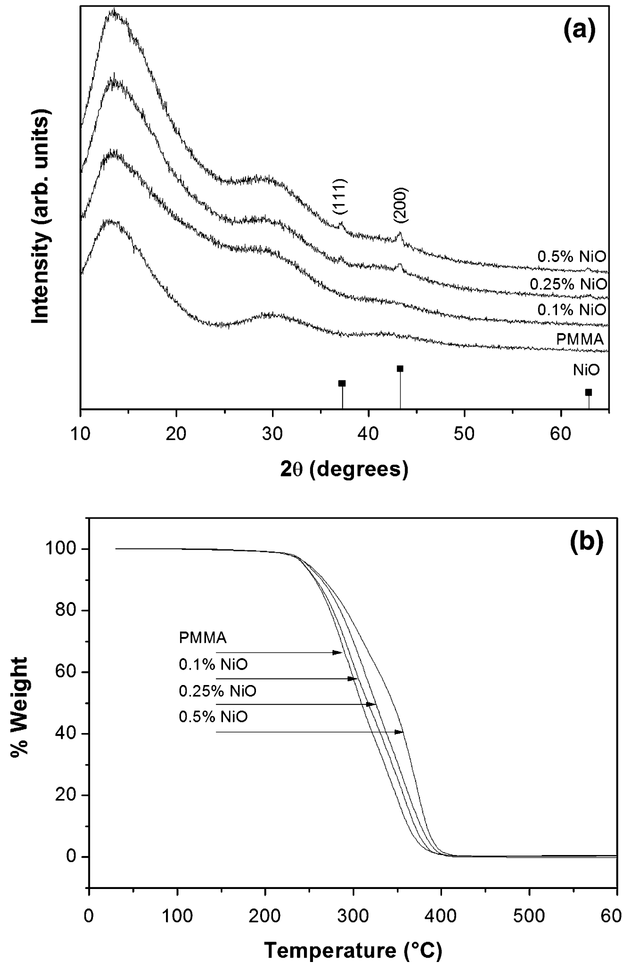

Fig. 4 XRD patterns (**a**) and thermogravimetric curves (**b**) of PMMA and PMMA/NiO nanocomposites with different amounts of NiO nanoparticles

in the presence of NiO nanoparticles. The NiO nanoparticles were prepared by Pechini method and its surface was modified with MPTMS. The results obtained from XRD indicate the formation of PMMA/NiO nanocomposites. The thermal properties of PMMA/NiO nanocomposites were investigated by TGA and compared to those of pure PMMA. From the results obtained, an improvement of the thermal stability of the nanocomposites was observed; the thermal stability increases in the presence of the NiO nanoparticles due to the restriction of mobility of the polymer chains. Currently, we are using these nanocomposites to prepare thin films on polymeric substrates for flexible electronic devices.

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