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Preparation and Magnetic Properties of Polyimide/Nickel Titanate Nanocomposite

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Polyimide/nickel titanate composite were successfully prepared through wet-chemistry synthesis method, using nickel titanate nanopowder and poly(amic acid). Pyrometallic dianhydride, 4,4-oxydianiline and *N,N*-dimethyl acetamide were used to prepare polyimide. In this method Fourier taransform infrared spectrometry, X-ray diffraction and scanning electron microscopy vibrating sample magnetometer were used to characterize the structure process, the particle size, morphology and the magnetic properties. The results indicated that polyimide/nickel titanate nanocomposite with particle size between 20 and 45 nm could be obtained after calcinations of the dried gel at 300 ºC for 1 h. The synthesized composites indicate a superparamagnetic behaviour, as observed by vibrating sample magnetometer at room temperature.

Key Words: Nanocomposite, Vibrating sample magnetometer, Nickel titanate, Polyimide.

INTRODUCTION

A composite consisting of a polymer matrix and dispersed ceramic particles is a kind of substance with great potential properties and applications[1]. Titanium based oxides containing metals such as $MTiO_3$ (M: Ni, Pb, Fe, Co, Cu and Zn) are universally known as inorganic functional materials with wide applications[2]. Nickel titanate has been investigated as a tribological coating to reduce friction and wear at high temperature applications without using liquid lubricants[3]. The wet-chemistry synthesis technique used in this study, including sol-gel, sol-precipitation, combustion synthesis, chemical coprecipition and hydro-thermal synthesis, offers many distinctive advantages over solid-state method in the production of powders such as controlled morphology, narrow size distribution and high purity[4-8]. Aromatic polyimides exhibit many useful properties such as high transition temperatures, excellent dimensional stability, low dielectric constants and outstanding thermal and thermo-oxidative stability. Therefore, some of these materials are used in such applications as high performance structural materials and packaging in printed electronic circuit. Polyimides are primarily used in the aerospace and microelectronics industries in the forms of films, moldings and foams[9]. Iron, cobalt and nickel are archetypal ferromagnetic metals. In bulk, electronic conduction in these materials takes place mainly through the *s*- and *p*-electrons, whereas the magnetic moments are mostly in the narrow *d*-electron bands, where they tend to align[10]. The oxide-based magnetic nanoparticles have been studied by many researchers because of their interesting particular magnetic properties such as superparamagnetic relaxation phenomena, surface effect by spin-canted structure, magneto-electrical transport and some other properties. They also have immense potential for applications in the areas of high-density data storage, ferrofluids, magnetic resonance imaging, colour processing and magnetic refrigeration. The superparamagnetic behaviour has often appeared in the magnetic nanoparticles with a few nano-meters[2].

EXPERIMENTAL

Nickel titanate ($NiTiO_3$) nanoparticles were prepared by a modified wet-chemistry synthesis method which is described in the literature[3]. In this way, a fixed amount of nickel stearate was added to the melted stearic acid and dissolved. Then, stoichiometric tetrabutyltitanate was added to the solution, stirred to form sol, naturally cooling down to room temperature and being dried to obtain dried gel. Finally, the gel was calcined at 750 ºC in air to obtain nanopowders of $NiTiO_3$.

Polyimide/nickel titanate composites were prepared along a synthetic procedure as summarized in Fig. 1. A solution containing 1 g-coupling agent of γ-aminopropyl triethoxysilane (APTS) in ethanol (5 mL) and 1 g nickel titanate particles were mixed in a flask under vigorous stirring. This suspension was ultrasonicted at room temperature for 10 min and heated at 80 ºC for 1 h. The condensation between pyrometallic dianhydride, 4,4-oxydianiline in *N,N*-dimethyl acetamide at room temperature was synthesized by reported method[6]. After adding the modified

$NiTiO_3$ particles into *N,N*-dimethyl acetamide, temperature yielded a poly(amic acid) (PAA, the precursor of polyimide) solution with certain solid content. Then, the mixture was vigorously stirred under ultrasonication for 4 h at room temperature giving a suspension. Then, the above poly(amic acid) solution was added into this suspension and was stirred for 24-48 h at temperature of 80 ºC and rate of 400-500 rpm and finally the dried gel was heated at temperatures to obtain (at each temperature of 100, 200, 250 and 300 ºC for 1 h, respectively), the polyimide/nickel titanate composites. In this process, the content of $NiTiO_3$ in the composite was controlled by the portion ratio of $NiTiO_3$ and poly(amic acid). The FTIR spectrum was recorded with an MB100 (BOMEM) spectrometer by using KBr pellet. The XRD patterns of the powders were recorded on Model PTS 3003 of SEIFERT diffractometer using CuK_α radiation (λ = 1.5418Å) in the ranges from 200 to 700 (2θ) to examine the crystallization and structural development of composites. The phase morphology of the composites was imaged by a scanning electron microscopy SEM Model VEGA of TESCAN. The magnetic measurements of composites was determained by vibrating sample magnetometer Model BHV-55.

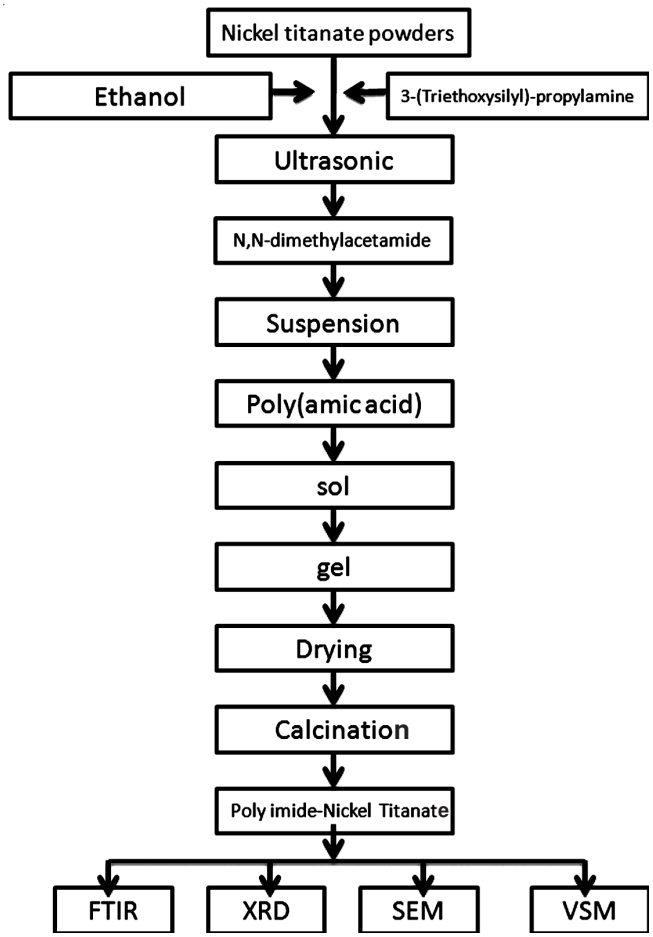

Fig. 1. Flow chart for the preparation of polyimide-$NiTiO_3$ nanocomposites

RESULTS AND DISCUSSION

X-ray diffraction patterns and IR spectra: Fig. 2 is the FT-IR spectra of polyimide/nickel titanate composite. In this spectrum the $NiTiO_3$ powder calcined at 750 ºC for 2 h showed peaks below 800 cm^{-1} which are assigned to the Ti-O stretching vibration[2]. In the spectrum of pure polyimide, the absorptions of imide carbonyl band at 1780 and 1720 cm^{-1} and the absorption of imide C-N band at 1380 cm^{-1} were the characteristics of pyrometallic dianhydride/4,4-oxydianiline polyimide[9].

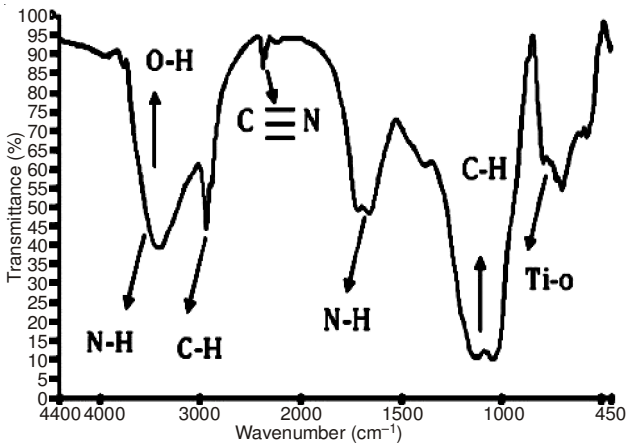

Fig. 2. FTIR spectra of the nanocomposites calcined at 300 ºC

In the spectrum of polyimide/nickel titanate composite, the absorption of $NiTiO_3$ below 800 cm^{-1}, as well as that of polyimide was found unchanged. These results show the successful synthesis of polyimide/nickel titanate composites. To investigate the stability of crystal structure of $NiTiO_3$ in the process of composite preparation, XRD measurements were carried out. Fig. 3 shows the XRD patterns of the original $NiTiO_3$ particle, the pure polyimide and the obtained polyimide/$NiTiO_3$ composite. It shows that the $NiTiO_3$ particles possessing a crystal rhombohedral structure[2] had no obvious differences in comparison with the pure $NiTiO_3$ in the composite. It also indicates that the crystal structure of $NiTiO_3$ was still stable when it was doped into polyimide matrix. However, the XRD pattern of polyimide matrix in the composite was different from that in pure polyimide. In the XRD of pure polyimide, the broad peak with 2 centers at 17.5 revealed that the polyimide molecules have amorphous structure. As well, this peak becomes narrow in comparison with the correspondence at 17.5 in pure polyimide.

Morphology of samples: The morphology of the composites which was measured by SEM is shown in Fig. 4. It

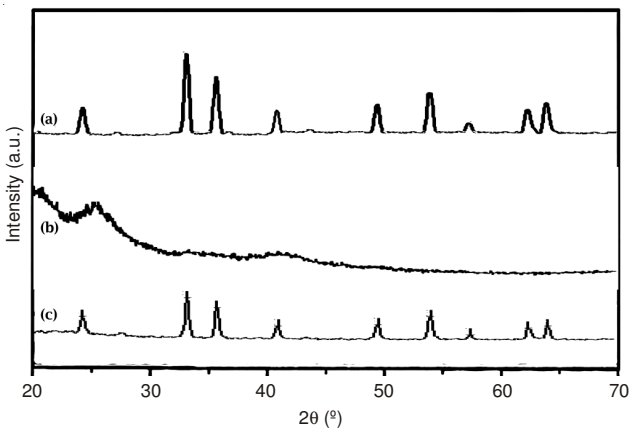

Fig. 3. X-ray patterns of (a) $NiTiO_3$ particles, (b) pure polyimide and (c) polyimide/$NiTiO_3$ ($NiTiO_3$ content is 10 %)

shows that $NiTiO_3$ particles were uniformly distributed throughout the polyimide matrix. There was no obvious aggregation of $NiTiO_3$ particles in the composites. The discrete phase remained semispheric shaped with diameters of 20-45 nm.

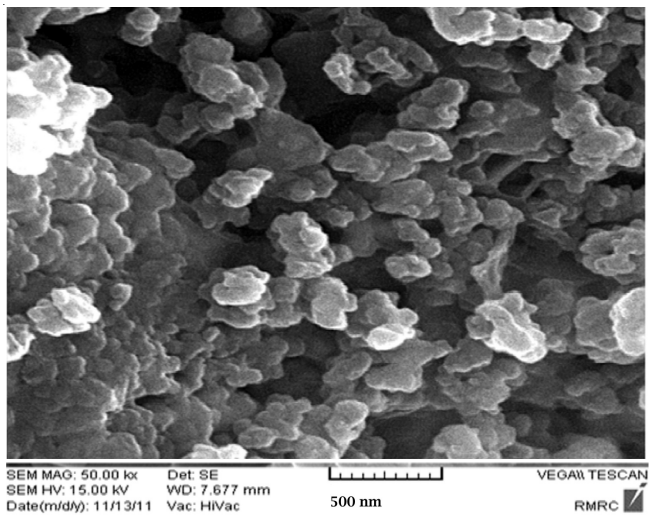

Fig. 4. SEM images of polyimide-$NiTiO_3$ nanocomposites calcined at 300 ºC

Magnetic properties: There are few reports regarding magnetic properties of $NiTiO_3$. The vibrating sample magnetometer was used for the magnetic measurements for the $NiTiO_3$ Fig. 5a show the magnetic properties of nanoparticles calcined at 750 ºC for 2 h. In the face-centered cubic crystallographic structure, the magnetic interactions of neighboring Ni^{2+} spins are ferromagnetic within the a-b planes and antiferromagnetic between adjacent a-b planes. The sample exhibits a fully reversible transition, representive of a genuine antiferromagnet. This fact reflects the good sample quality, since magnetic irreversibilities are often present in magnetic ceramic samples. The synthesized $NiTiO_3$ indicates a superparamagnetic behaviour, as evidenced by zero coercivity and remanance on the magnetization loop. The system of superparamagnetic particles do not show hysteresis in the M-H curves. Hence HC and MR are near zero. A saturation magnetization of *ca*. 0.2 emu/g. The vibrating sample magnetometer magnetic measurements for the polyimide/nickel titanate Fig. 5b shows the magnetic properties of nanocomposites calcined at 300 ºC for 1 h. The results showed that the saturated magnetization (Ms) of the polyimide/$NiTiO_3$ nanocomposites was 0.06 emu/g and its saturated magnetic strength was 10000 Oe. In other words, when the particle is small enough and the anisotropy energy is too small to be identical with the heat motion, the direction of magnetization would no longer be fixed and the direction of easy magnetization would change irregularly, causing the super paramagnetic phenomenon.

This study has demonstrated the feasibility of synthesis of polyimide/$NiTiO_3$ nanocomposites using wet chemistry synthesis and stearic acid gel methods. Well crystallized polyimide-$NiTiO_3$ nanocomposites could be synthesized at 300 ºC for 1 h. Morever, the synthesized polyimide/$NiTiO_3$ indicated a superparamagnetic behaviour, as observed by vibrating sample magnetometer at room temperature.

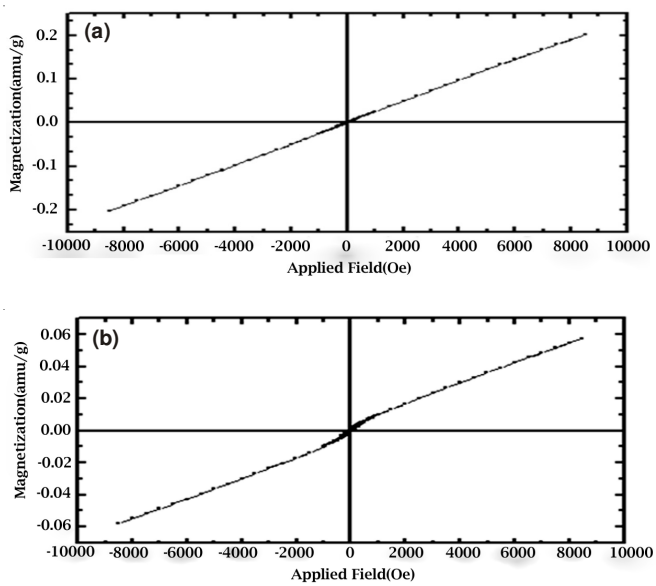

Fig. 5. VSM curves of a) $NiTiO_3$ nanoparticles calcined at 750 ºC, b) polyimide-$NiTiO_3$ nanocomposites calcined at 300 ºC

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