



Fabrication and properties of novel superparamagnetic, well – Dispersed waterborne Polyurethane/Ni–Zn ferrite nanocomposites



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ABSTRACT

Novel superparamagnetic nanocomposites based on covalently linked waterborne polyurethane (WPU) and $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ ferrite nanospheres (NZFO) were successfully synthesized using an *in situ* polymerization method. The $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles prepared by a typical solvothermal method were modified with 3-(triethoxysilyl) propyl isocyanate (IPTS) to improve the compatibility with monomers. The functionalized NZFO nanoparticles (NZFO-IPTS) served as effective cross-link points and reacted with the WPU matrix, forming chemical bonds. It was found that the NZFO-IPTS greatly improved the dispersibility of NZFO nanoparticles in the WPU matrix, and the introduction of NZFO-IPTS enhanced the thermal behavior and mechanical properties of the WPU polymer. What's more, the WPU/NZFO nanocomposites presented superior magnetic properties and a maximum saturation magnetization (M_s) of 16.58 emu/cm^3 was observed, thus illustrating the potential applications of the generated materials in microwave-absorbing fields.

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1. Introduction

Polymer-inorganic nanocomposites have recently attracted considerable attention in both industry and academia, because compared to pure polymers or conventional micro-composites, they often not only improve the performances of materials, such as barrier properties, solvent resistance, and tensile properties [1–3], but also endow polymers with other special functionalities, including conductivity, optical properties, bio-catalysis etc [4–6]. To date, oxides like SiO_2 [7], Al_2O_3 [8], layered silicate like kaolinite [9], carbon materials like MWCNTs [10], and graphene [11], have been used as fillers in various polymer matrices.

Water-based systems have started to dominate the coating market due to their lower toxicity as compared to the solvent-based products. Waterborne polyurethane (WPU) is a new branch of polyurethane (PU) system which water is used in place of traditional organic solvents (toluene, acetone), thus largely reducing the release of volatile organic compounds (VOCs) [12]. Compared to conventional PUs, WPU exhibits numerous prominent advantages, such as high adhesion, good compatibility, flexibility, non-pollution

etc. Therefore, numerous applications of WPU in coatings, adhesives, and biological products have come about in recent decade years [13]. However, most commercial waterborne polyurethane are linear thermoplastic polymers with polar groups in the chain backbone. Therefore, the mechanical properties, thermal stability, and solvent resistance are much lower than those of solvent-based PUs. In order to address this issue, some measures have been taken, including gave a higher degree of cross-linking of waterborne polyurethane and added various inorganic nanoparticles to polymer matrix [14]. Nevertheless, previous works have mostly reported WPU nanocomposites that were prepared by simple physical mixing without attachments for other special functions. Furthermore, the particles easily aggregated, which has a negative influence on the properties of the final materials [15,16].

Over the past several decades, magnetic metal oxides have been widely studied due to their superparamagnetism, high biocompatibility, and low toxicity. In line with this trend, nickel zinc magnetic nanoparticles have drawn remarkable attention because of their wide range of potential applications, such as in microwave absorption materials, biocatalysis, and high-density information storage [17–19]. Based on the superior magnetism, good mechanical abrasion resistance, chemical stability etc., Ni–Zn ferrite has been used as a filler and has been added in different polymer

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matrices to form composites [20,21]. Nanocomposite based on waterborne polyurethane and Ni–Zn ferrite shows excellent magnetic properties, and can be widely used to reduce the electromagnetic reflections of particular devices such as aircrafts and ships for less susceptibility against radars, and can be used for the interior covering of anechoic chambers [22]. However, Ni–Zn particles have not received much attention as a filler for their unique magnetic functions of WPU, potentially because Ni–Zn nanoparticles easily agglomerate during mechanical mixing process, which would have a negative effect on the physical properties of the final composites. Further, as compared to other inorganic particles, the high density of Ni–Zn ferrite constitutes another problem, as it would lead to poor emulsion stability of WPU/Ni–Zn ferrite composites, unless strong interactions have been formed between WPU and Ni–Zn particles. In short, adding Ni–Zn ferrite in a WPU matrix not only improves physical properties of polymer, but can also confer excellent magnetic properties on the nanocomposites.

In this study, a nano-scale $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ powder was first prepared by a solvothermal method, and then modified with IPTS to prevent agglomeration and improve compatibility with the monomers. Since the functionalized NZFO nanoparticles (NZFO-IPTS) can be combined with other components that used for WPU synthesis through covalent bonds on one hand. Moreover, NZFO-IPTS nanoparticles can serve as effective crosslink points, which would play an important role in the improvement of the nanocomposite performance. The morphology, microstructure, as well as thermal, magnetic and mechanical properties of the WPU/NZFO nanocomposites were characterized and investigated.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), poly (propylene glycol) (PPG-2000) and trimethylolpropane (TMP) were supplied by Sinopharm Chemical Reagent Co. Ltd (China). Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium acetate (NaAc) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd (China). Zinc chloride (ZnCl_2), ammonium acetate (NH_4Ac) and triethylamine (TEA) were obtained from Tianjin Guangfu Technology Development Co. Ltd (China). 3-(triethoxysilyl) propyl isocyanate (IPTS) was supplied by Ladder Hope Love Chemical Industry Development Co. Ltd (China). Isophorone diisocyanate (IPDI), diethylene glycol and ethylene glycol were purchased from Shanghai Chemical Reagents Corp. (China). Polyvinylpyrrolidone (PVP, K30) and hydroxyethyl methacrylate (HEMA) were obtained from Tianjin Institute of Chemical Reagents (China). Dibutyltin dilaurate (DBTDL) and Irgacure 2959 were purchased from Tianjin Kaixin Chemical Co. Ltd (China). Dimethylol propionic acid (DMPA) was supplied by Aldrich Chemical (China) and dried under vacuum for 24 h at 80 °C. All reagents were of analytical purity.

2.2. Synthesis of nearly monodisperse NZFO and NZFO-IPTS nanoparticles

The $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles were prepared as follows: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1/5 mmol), ZnCl_2 (7/15 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (4/3 mmol) were dissolved in a mixture of diethylene glycol (19 mL) and ethylene glycol (1 mL) under magnetic stirring. 1.00 g of PVP was added and the suspension was heated at 120 °C for about 1 h to form a transparent solution. Subsequently, 1.50 g of NaAc was introduced into the solution. The final solution was transferred to a Teflon-lined autoclave and was calcined at 200 °C for 12 h. The resulting NZFO product was washed with ethanol and water several times, and then dried under vacuum for 12 h at 40 °C. To prepare

NZFO-IPTS nanoparticles, 0.40 g of the NZFO powders were first dispersed in 40 mL of toluene in a dry flask under a flow of N_2 and mechanical stirring. After 0.5 h, 2 mL of 3-(triethoxysilyl) propyl isocyanate (IPTS) was added to the solution and the system was heated to 120 °C and allowed to react for 36 h. The product was washed with toluene and acetone and dried under vacuum at 40 °C for 24 h.

2.3. Preparation of WPU/NZFO nanocomposite films

The WPU/NZFO emulsion was prepared as follows: in a dry flask equipped with a N_2 inlet, PPG-2000 (5 mmol) and DMPA (5 mmol) were added under mechanical stirring. IPDI (20 mmol) and 0.3 wt % of DBTDL were introduced into the solution and the system was heated at 80 °C for 3 h. Subsequently, the solution was cooled to 60 °C and 20 mmol of HEMA was added at 60 °C for 2 h. Stoichiometric amount of NZFO-IPTS was added to the solution and kept ultrasonic for 2 h. Later, the system was heated to 60 °C and 5 mmol of TMP dissolved in acetone was added, and the mixture was allowed to react for another 2 h. The mixture was neutralized by addition of TEA at 40 °C. Finally, a certain amount of water was added to emulsify the neutralized dispersion, and it was stirred for 40 min at 40 °C. The solid content of the final WPU/NZFO nanocomposite emulsion was 40%. The WPU/NZFO film was prepared by mixing preweighted above emulsion with 3 wt % of Irgacure 2959 in a dry flask. The homogenous dispersion was spread on a Teflon plate surface and allowed to stand at room temperature for 12 h to remove most of the water before curing. Finally, the film was obtained by exposing the Teflon plate with dispersion under UV light to cure for 4 min. Films with NZFO-IPTS mass fractions of 0, 0.5, 2, 4, 6, and 8 are marked as WPU, WPU/NZFO-0.5, WPU/NZFO-2, WPU/NZFO-4, WPU/NZFO-6, and WPU/NZFO-8, respectively. The synthetic process is shown in Scheme 1.

2.4. Measurements

The morphology of the NZFO nanoparticles and WPU/NZFO films were characterized by transmission electron microscopy (TEM, FEI Tecnai G20) and scanning electron microscopy (SEM, JSM-6380Lv, JEOL, Japan; JSM-6701F, JEOL, Japan). X-ray power diffraction (XRD, Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation) was used to identify the crystal structure of the products. The FTIR spectra were recorded on a spectrophotometer (American Nicolet Corp. Model 170-SX), the sample and KBr were pressed to form a tablet. The TGA curves were obtained using a TA Instrument (NETZSCH STA 449C) at temperatures ranging from room temperature to 800 °C. Dynamic Mechanical Analyzer (DMA, Mettler-Toledo) was conducted from –50 to 200 °C (the size of sample was 9 mm × 4 mm × 0.4 mm) to investigate the thermal mechanical behavior. A drawing machine (Instron1122) with a drawing speed of 30 mm/min was utilized to confirm the mechanical properties according to the national standard GB1447-83. The magnetic properties were measured by vibrating sample magnetism (VSM, LAKESHORE-7304, USA).

3. Results and discussion

3.1. Morphology and microstructure of NZFO and WPU/NZFO nanocomposites

The morphologies of the NZFO particles and WPU/NZFO films were investigated using TEM and SEM. Fig. 1a shows the TEM image of NZFO particles. The particles were spherical with the diameters ranging from 15 nm to 20 nm. Fig. 1b–e show the SEM micrographs of cross-sections of the film products. Pure WPU exhibited a

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