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A systematic study of maghemite/PMMA nano-fibrous composite via an electrospinning process: Synthesis and characterization

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ABSTRACT

In this study, maghemite/PMMA nano-fibrous composites have been successfully fabricated by using the electrospinning process. PMMA nano-fibres have been selected to be used as the matrix; the PMMA was dissolved in three diverse solvents (Acetone, THF and DMF) in order to obtain fine PMMA nano-fibres. As a result, the PMMA–DMF proved to be the most appropriate polymer solution among the three solvents, with its impressive defect-free surface morphology results. The production of maghemite using Massart's procedure resulted in nano-particles with an average diameter of 4.98 ± 0.13 nm (using transmission electron microscopy (TEM)). Maghemite nano-particle were then mixed with a prepared polymer solution in order to fabricate maghemite/PMMA nano-fibrous composite. Furthermore, the investigation of the morphology and structure of the composite was carried out using field emission scanning electron microscopy (FESEM), Energy-dispersion X-ray spectroscopy (EDX), Alternating Gradient Magnetometer (AGM), Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD) and tensile strength measurement devices. The results indicated that there was a great amount of maghemite, both in and on the composite's surface, which can be utilized in the purpose of magnetic applications.

1. Introduction

At the present time, there is a persistently growing demand to produce micro or nano-scales fibres due to their exceptional and considerably unique properties [1]. Over the past years, several processes have been introduced to meet this requirement [1]. Electrospinning is one of these processes which has been highly fascinating to scientists in recent decades, because of its ability to produce uniform fibres, in both micro and nano-scales [2,3]. In addition, these fibres can be effectively produced in different scales by adjusting the electrospinning parameters [4]. Accordingly, the fibres appear to possess a highly specific surface area, appropriate surface morphology [5,6], satisfactory shape [7] and specific chemical and physical properties [8]; with the capacity to carry versatile particles for diverse applications such as filtration [9], drug delivery [10] and biomedical [11] applications.

In order to fulfil a number of requirements in the industry [12,13], there are a number of nano-particles, and magnetic nano-particles, particularly maghemite, which is one of the most extensively used among them [13,14]. The

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magnetic nano-particles serve as an inspiration for a more intense interest in research, particularly in the area of treating polluted water [15] or subsurface environments using engineering applications [13]. Researchers have proposed different methods for fabricating magehmite particles with reference to their size, shape, surface morphology and structural properties [16–19]. It has also been established that the properties of maghemite found to have a high dependence on size [20]. Clark et al. [21] have demonstrated that the magnetic properties of maghemite has a remarkably more applications when the size of the particles is smaller, particularly less than 10 nm. There are other factors such as temperature, external magnetic field, size distribution and degree of inter-particle interactions which affect the effectiveness of the applications [13]. Markedly, many scholars have concluded that the particle size is the most effective parameter in the performance of magnetic particles [22–25]. As a result, it has been highly recommended for diverse applications such as filtration [15], drug delivery [26] and biomedicine [27–29].

Tang et al. [13] reported that in several applications of magnetic particles, there was a lack of efficiency in some applications. For example, Petosa et al. [30] found that the aggregation of particles decreases removal capacity and reactivity, thereby limiting the overall removal performance. Several conditions leading to the aggregation of magnetic nano-particles are highlighted, including the particle size distribution, particle concentration, solution composition, surface chemistry, and certainly the magnetism of the nano-particles [8,13,30]. One of the popular alternative solutions to these problems is using an appropriate nano-scale matrix.

The process of dispersing nano-particles into the fibres has been executed to increase the capacity of the composites in each given application [31–33]. Polymethyl Methacrylate (PMMA) was selected as a matrix and has been frequently the material of choice for outdoor applications, due to its specific properties, for example, having superior environmental stability [34,35] in comparison with most other plastics, specifically polystyrene and polyethylene [1,31,36]. The combination of nano-materials and PMMA nano-fibres is a subject which has been comprehensively deliberated in some collected works, i.e. in the case of noble metals [37–39], magnetic [40] or luminescent nano-particles [41].

The purpose of the study is to determine the feasibility of incorporating super-paramagnetic nano-particles with electrospun nano-fibres, which has been an existing bottleneck to date. Then, with the aim to prove the formation of maghemite/PMMA nano-fibrous composite, EDX, AGM, FTIR and XRD were employed; and later, in order to study the morphology and distribution of maghemite nano-particles in the nano-fibres, FESEM imaging was also used. In addition, tensile strength was used to evaluate the effect of maghemite in altering mechanical properties. In this work, the authors added magnetic nano-particles onto a PMMA matrix before the formation of the fibres (which could also be formed by using electrospinning).

2. Materials and methods

2.1. Synthesis of maghemite nano-particles

In this research, maghemite nano-particles were synthesized by the process of chemical co-precipitation of ferric and ferrous ions in an alkaline solution, known as Massart's procedure [17]. Aqueous solutions of $FeCl_24H_2O$, which is stabilized by adding a few drops of HCl and $FeCl_36H_2O$, were mixed at a molar ratio of 2:1 for Fe^{3+}:Fe^{2+}. In addition, a large amount of ammonium hydroxide (NH_4OH) was added to the solution in order to guarantee the completion of the precipitation process. Then, adding NH_4OH to the solution resulted in the instantaneous formation of black precipitates. Subsequently, the clear supernatant was dispensed after the precipitates settled at the bottom of the beaker. After that, the process of washing the precipitates with deionized water was repeated 6 times. It was followed by stirring the precipitates in a nitric acid solution (HNO_3). The nitric acid serves as an oxidizing agent and plays an important role to dissolve the remaining iron oxide into maghemite. Then, these particles were heated at 90 °C in ferric nitrate solution to complete the oxidation. Next, the particles were sequestered and then peptized in deionized water. Finally, by conducting the process of drying the suspension in an oven at a slightly elevated temperature, the powder specimens were obtained.

2.2. Electrospinning of maghemite/PMMA nano-fibrous composite

Additionally, the analytically pure Polymethylmethacrylate (PMMA, $(—CH_2C—(CH_3))CO_2CH_3)—$), M_w = 120,000) from Aldrich was used as the polymer in this study. By dissolving 15 wt.% PMMA in Acetone, then in Tetrahydrofuran (THF) and finally in N,N-dimethylformamide (DMF) solvent, the polymer solution samples were obtained. All these solvents were obtained from Labchem Sdn Bhd Co., Malaysia. The process was conducted by dissolving an adjusted quantity of PMMA in the different solvents through vigorous stirring for a period of twenty-four hours.

In order to perform the electrospinning process, a 5 ml plastic syringe with a needle gauge No. 19 was utilized in which to place the polymer solution. The ES30P-30W/SDPM (Gamma High Voltage Research, Ormond Beach, FL) was used as the direct source of high voltage power. The expected Taylor cone was produced during experimentation by using an appropriate amount of voltage (23 kV). A high voltage power source was connected to the needle through an alligator clip. Then, a ground target covered with aluminium foil was used as the counter electrode, at tip-to-distance, which was fixed at 15 cm. Moreover, a syringe pump (NE-300, New Era Pump Systems, Inc.) was used in order to control the feed rate of 4 ml/h.

In view of the fact that the choice of the temperature and relative humidity are both important, the electrospinning process was performed at 25 °C and 32% RH [42].