Industrial Crops & Products 111 (2018) 47–54

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Research paper

Superparamagnetic Fe_3O_4@ wood flour/polypropylene nanocomposites: Physical and mechanical properties

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ARTICLE INFO

Keywords:
Wood-plastic nanocomposite
Magnetic wood flour
Polypropylene
Physical properties
Mechanical properties
Superparamagnetic Fe_3O_4 nanoparticles

ABSTRACT

Given the high potential applications of magnetic green polymer nanocomposites in the construction, automotive and military industries, fabrication and characterization of superparamagnetic Fe_3O_4@ wood flour/polypropylene nanocomposites were investigated for the first time in this study. Magnetite (Fe_3O_4) nanoparticles were in situ synthesized on poplar wood flours. The filler loading used was 40 wt.% and the virgin wood flours (VWFs) and magnetic wood flours (MWFs) were used as filler at three levels of mixing ratios (VWFs: MWFs = 100:0, 50:50, and 0:100 wt.%). Maleic anhydride-grafted PP (MAPP) was used as the MAPP at two levels of 1 and 3 wt.%. Characterization of the MWFs confirmed the successful "in situ synthesis" of spherical superparamagnetic Fe_3O_4 nanoparticles on the wood flours with an average crystal size of about 8 nm at approximately 30 wt.%. The physical properties examinations indicated that the increase of MWFs up to 100 wt.% of filler phase increased the long-term water absorption and thickness swelling of specimens up to 2.6 and 2.4-fold, respectively. The ultimate tensile and flexural strengths increased when MWFs increased by up to 50 wt.% and then decreased at higher weight ratios of MWFs. Increasing the MAPP from 1 to 3 wt.% improved both physical and mechanical properties, but this effect was more perceptible in improving mechanical strengths compared to the elastic modulus. The magnetization characterization showed about 10% reduction in saturation magnetization (M_s) of the final MWFs/polypropylene nanocomposites in comparison with the M_s values of the starting MWFs (≈1 emu/g). This observation was attributed to the formation of a nonmagnetic layer on the Fe_3O_4 nanoparticles during the melt-blending process.

1. Introduction

For about three decades now, wood-plastic composites produced by mixing industrial polymers such as polyethylene, polypropylene, polyvinyl chloride, and polystyrene with lignocellulosic fillers in various geometrical shapes and dimensions have been the focus of interest of large industries, especially the construction and automotive industries (Holbery and Houston, 2006; Klyosov, 2007; Koronis et al., 2013; La Mantia and Morreale, 2011; Martins et al., 2016; Nourbakhsh et al., 2011; Selke and Wichman, 2004; Smith and Wolcott, 2006; Taşdemır et al., 2009). Wood-plastic offers less water absorption, greater dimensional stability, and more resistance to biological degradation and weathering compared to untreated solid wood (Klyosov, 2007; Rowell et al., 1997; Selke and Wichman, 2004; Wechsler and Hiziroglu, 2007). Furthermore, it has modification capability which commensurate with the desired applications and mechanical strength, as well as the required densities. In general, compared to untreated solid wood, wood-plastic composite is a greener, more cost-effective and more efficient product mainly due to the fact that it can combine the superior features of natural fibers such as being environment-friendly, abundant, inexpensive, non-corrosive, low density, and low coefficient of thermal expansion with desirable mechanical characteristics in addition to those of the synthetic polymers, including resistance to water absorption, thickness swelling, and biological degradation, and ease of processing as well as plasticity in complex three-dimensional shapes (Hosseinaei et al., 2012; Klyosov, 2007; Mohanty et al., 2005; Rowell et al., 1997; Stark and Rowlands, 2007; Tajvidi et al., 2006; Wang et al., 2006; Wechsler and Hiziroglu, 2007; Yang et al., 2006). In addition to the warm reception of this product by large construction and automotive industries, developmental studies have boosted towards given objectives such as upgrading quality and customizing features of wood-plastic composites that commensurate with their final applications.

The advent of nanotechnology has influenced the surging development of industrial products and wood-plastic industry was no exception. Many researchers in this field have attempted to tackle issues such as upgrading the quality and range of the applications of their products

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http://dx.doi.org/10.1016/j.indcrop.2017.09.068
Received 14 May 2017; Received in revised form 29 September 2017; Accepted 30 September 2017

by utilizing this technology (Borah and Kim, 2016; Hosseini, 2016; Saba et al., 2016; Saha and Sutradhar, 2016). Production of wood-plastic products with much greater superiority in features of scratch, stain, fire and moisture resistance, resistance to biological agents and weathering, and of having lighter weight together with superior mechanical and engineering features are among some goals of employing nanotechnology in this industrial field (Ashori et al., 2013; Ayrilmis et al., 2014; Borah and Kim, 2016; Faruk and Matuana, 2008; Guo et al., 2007; Hosseini, 2016; Karakuş et al., 2017; Kordkheili et al., 2013; Najafi, 2013; Rasouli et al., 2016; Saba et al., 2016; Saha and Sutradhar, 2016). Reports of extensive research on the use of mineral nanoparticles such as various types of nanoclay, zinc oxide, titanium dioxide, nanosilicate and other types of nano oxides and mineral hybrids with the purpose of quality improvement and creation of special applied features in wood-plastic composites have been published in recent years (Deka and Maji, 2013; Faruk and Matuana, 2008; Guo et al., 2007; Hosseini, 2016; Nourbakhsh et al., 2011; Rasouli et al., 2016; Saba et al., 2016; Wang et al., 2015; Ye et al., 2016). Magnetic nanoparticles including iron, nickel, manganese, cobalt oxides, and their hybrids are among the most attractive members in the family of mineral nanoparticles and numerous potential applications have been predicted for them in various electronic, military, and medical industries (Frey et al., 2009; Kodama, 1999; Willard et al., 2004). During the past two decades, studies have been reported on manufacturing and evaluation of the properties of magnetic wood as an efficient material in electromagnetic shielding and indoor electromagnetic wave absorption (Gan et al., 2015; Oka and Fujita, 1999; Oka et al., 2004; Oka et al., 2002a; Oka et al., 2007; Oka et al., 2002b; Oka et al., 2012; Oka et al., 2011). Considering these features, magnetic wood can be used as a functional engineering material especially in the construction, automotive and military industries with the aim of preventing interference and leakage of electromagnetic waves. With regard to the advantages mentioned for wood-plastic composites compared to solid wood, for the first time, this research aimed to fabricate superparamagnetic Fe_3O_4@ wood flour/polypropylene nanocomposites and evaluate their physical and mechanical features. Review of literature showed that no report has hitherto been published on the manufacturing of magnetic wood-plastic composite or on evaluation of its features. Therefore, it is expected that results of the present research will be a first step in the manufacturing and development of a new generation of functional wood-plastic composites with desirable magnetic properties to be used in construction, automotive, and military industries.

2. Materials and methods

2.1. Materials

Poplar (Populus deltoides) wood flour was used as the lignocellulosic filler. Injection grade polypropylene (V30S, MFI = 18 g/10 min, density = 0.92 g/cm) produced by Petrochemical Company of Arak in Iran was used as the continuous phase. Furthermore, maleic anhydride coupled with polypropylene (MAPP) grade PP-G 101 (Kimya Javid Sepahan Co., Isfahan, Iran) was employed to enhance compatibility of the matrix phase with the filler. The melt-flow index of the MAPP was 100 g/10 min. Ferrous chloride tetra-hydrate ($FeCl_2{\cdot}4H_2O$), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and sodium hydroxide (NaOH) were purchased from Daejung Chemicals and Metals Co. (Korea). All chemicals used were of analytical grade and were used as received without further purification.

2.2. Methods

2.2.1. Preparation and hydrothermal pretreatment of wood flour

Poplar wood shavings were first prepared using a wood chipping machine. The shavings were dried at 103 ± 2 °C and a laboratory mill was employed to turn them into wood flour particles. Laboratory sieves were then used to separate 60-mesh wood flours to be further used as the filler phase.

Prior to the in situ synthesis of Fe_3O_4 nanoparticles, the wood flours were exposed to a mild hydrothermal treatment to prevent possible effect of contaminations, and extracted materials were dissolved in water. Since the temperature in the in situ synthesis of magnetite nanoparticles was presumed to be at about 75 °C, the hydrothermal pretreatment was done in two 2-h stages in distilled water at 85 °C. At the completion of the pretreatment, the wood flours clearly had a visible lighter color.

2.2.2. Preparation of Fe_3O_4@ wood flour nanocomposite particles

In situ synthesis of Fe_3O_4 nanoparticles was performed with the reduction of iron (II) and iron (III) solutions in the presence of the pretreated wood flour particles. The hydrothermal pretreated wood flours were immersed in twice the volume of double distilled water inside a laboratory reactor equipped with a mechanical stirrer and constant flow of the inert nitrogen gas and heated at 65 °C for one hour. The flow rate of the nitrogen gas was 10 L/min and the speed of the mechanical stirrer was 300 rpm for deoxygenation and maintenance of homogenous conditions inside the reactor until the completion of the hydrothermal synthesis. $FeCl_2{\cdot}4H_2O$ (0.06 mol/L) and $FeCl_3{\cdot}6H_2O$ (0.12 mol/L) were weighed and immediately added to the reaction mixture. In order for the dissolution to be completed and the penetration of metal cations into the wood flours to get thoroughly ended, we waited for two hours at this step. Afterwards, the wood flours were removed from the reaction environment, dehydrated immediately, and fed into another thermal chamber containing 1 M sodium hydroxide under the same hydrothermal conditions, nitrogen gas flow rate, hydrothermal duration and mechanical stirrer speed for the reduction process of the metal cations and the in situ synthesis of magnetite nanoparticles to take place. The prepared black Fe_3O_4@ wood flour nanocomposite particles were removed from the reaction environment and washed several times to remove the excess nanoparticles and the chemicals that had not taken part in the reactions. The magnetic wood flours (MWFs) were first dehydrated thoroughly using the mechanical method and then dried in two 24 h stages (first at about 60 ± 2 °C and then at 103 ± 2 °C). The prepared MWFs were poured into 2-layered polymeric bags that were completely sealed to prevent moisture absorption until they were properly mixed with the matrix phase.

2.2.3. Combination of MWFs and polymer matrix

The abbreviated code and weight percent ratio of the combination in each formulation are presented in Table 1. The materials in dry form and with known weight percentages in each formulation were first thoroughly mixed, and the melt mixing and granule production processes were then carried out using a Dr. Collin counter-rotating twin screw extruder/compounder machine (Dr. Collin GMBH, Germany) with four temperature zones with the maximum and minimum temperatures of 165 and 150 °C and speed of 70 rpm.

2.2.4. Injection molding and test samples preparation

Prior to the injection molding process and preparation of final test samples, the granules were exposed to 103 ± 2 °C for 4 h to ensure complete removal of moisture. The final test samples were prepared

Table 1
Codes of the formulations and their compositions.

Formulation	PP (%)	VWF (%)	MWF (%)	MAPP (%)
PP-VWF40-MA1	59	40	0	1
PP-VWF40-MA3	57	40	0	3
PP-VWF20-MWF20-MA1	59	20	20	1
PP-VWF20-MWF20-MA3	57	20	20	3
PP-MWF40-MA1	59	0	40	1
PP-MWF40-MA3	57	0	40	3