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3-Aminopropyl-triethoxysilane-functionalized rice husk and rice husk ash reinforced polyamide 6/graphene oxide sustainable nanocomposites

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ABSTRACT

Rice husk and rice husk ash are two well-known sustainable materials for wastewater purification applications. In this work, functionalized-rice husk and -rice husk ash reinforced polyamide 6/ graphene oxide nanocomposites are fabricated using the solution casting method. 3-Aminopropyl-triethoxysilane is used as the functionalizing agent for the surface modification of rice husk and rice husk ash particles. Siloxane bonding between silanol groups of the functionalizing agent and silica containing particles can result in the introduction of amino groups on the surface of particles, which can react with either terminal carboxyl groups or amide groups of the polyamide 6. Functionalized-rice husk ash, which contains a large amount of nano silica, forms distributed nano-sized aggregates in the structure of the polyamide 6. Moreover, the simultaneous presence of graphene oxide and rice husk ash, as an organic/inorganic nano-system, in the matrix structure results in a clear enhancement in the structural and mechanical characteristics of final nanocomposites. This is the result of possible strong interactions between the polymeric matrix and the organic/inorganic nano-system. The influences of the organic/inorganic nano-system on the melting process, morphology and dynamic-mechanical properties of reinforced nanocomposites are investigated in details. Moreover, the impacts of the organic/inorganic nano-system loading on the thermal stability of fabricated nanocomposites are studied. Considering results presented here and the well-known adsorbent characteristics of rice husk ash nanoparticles, the functionalized-rice husk ash/graphene oxide/polyamide 6 sustainable nanocomposite is a perfect candidate for fabricating nanofibers, which are applicable in wastewater purification applications.

1. Introduction

Among different biomasses, rice husk (RH) is an important byproduct of the rice production industry, which can be used for the electricity production purposes through burning into rice husk ash (RHA) [1]. The waste product of an uncontrolled burning process (which is more often nowadays) is low quality RHA, which its disposal into landfills (due to poor quality, it is often dumped in

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landfills) can cause some serious environmental problems [2]. However, controlled burning of RH into RHA could, besides energy, leads to other value-added products, such as high-quality silica and nano silica, with purities > 99% [3]. With the increase of worldwide environmental concerns, and with the current increasing pattern of rice production and consumption [1], the necessity of novel solutions for the environmental problems of RH and RHA seems crucial. A widely interested potential solution to this issue is the employment of RH and RHA particles for the fabrication of metal-matrix [4], ceramic-matrix [5] or polymer-matrix [2] composites. Particularly, the incorporation of RH and RHA particles into polymeric systems is reported to result in the formation of advanced sustainable nanocomposites with enhanced properties [2,6]. In this way, on the one hand, RH and RHA particles can be reused in an industrial way, and on the other hand, sustainability can be rolled into the polymer engineering, which is a great perspective for the future of this important industry.

Main elements within the structure of RH are C (37.05 wt.%), O (35.03 wt.%), N (11.06 wt.%), Si (9.01 wt.%) and H (8.80 wt.%) [2]. The contents of cellulose, hemicellulose and lignin in the structure of RH are about 34.4, 24.3 and 19.2%, respectively [2]. Therefore, most of the RH structure is comprised of polysaccharides and consequently, RH, like other natural fiber systems, has a low compatibility with most of the polymeric systems [7]. Burning of RH results in formation of RHA, which is a sustainable source for silica nanoparticles [8,9]. Both RH and RHA particles are known to be superior adsorbent for heavy metals, dyes and other organic pollutants of water [2,6]. As a result, incorporation of these materials into polymer-based nanocomposite fibers can result in formation of nanofibers with excellent characteristics for wastewater purification applications.

Recently, different polymers (i.e. polyvinylidene, polysulfone, nylon 6, polyethersulfone, cellulose, polyacrylonitrile, etc.) have been successfully used for fabricating nanofibers with potential applications in the filtration [10]. Due to its high mechanical strength, chemical resistance towards a wide range of solvents and high stiffness, polyamide 6 (PA6) is a widely interested material for the production of advanced fibers and nanofibers [10,11]. PA6-derived nanofibers have been successfully employed for separating micron to sub-micron particles from wastewater [12,13]. Moreover, when filled with an appropriate nanomaterial (e.g. carbon nanotubes, graphene oxide, nano TiO_2, nano Ag, etc.), PA6-based nanocomposites have also a promising potential for the fabrication of advanced nanofibrous systems [14–17]. In particular, PA6/graphene oxide (GO) nanocomposites, not only present a proper achievable range of nano diameter through the electrospinning process [17], but also offer high structural stability and mechanical characteristics, even with the incorporation of very low amounts of GO [18–21].

When incorporated into a proper matrix, GO has been reported to be a perfect substrate for assembling high-efficient water treatment systems [22]. However, despite great efforts through recent years for the synthesis of GO through more affordable mechanisms, GO can be still classified into the category of expensive nanomaterials [23]. Therefore, reaching a high filtration-efficiency by employing GO as the only adsorbing agent may increase the final-price of wastewater treatment systems. However, despite expenses, due to its superior high available surface area, incorporation of GO nanosheets (even at very low amounts) results in a clear efficiency improvement of water treatment systems [24]. Consequently, and by considering the high performance of RH and RHA particles in adsorbing water pollutants, incorporation of RH/GO or RHA/GO inorganic/organic hybrid nano-systems can be considered as a solution for the discussed environmental concerns regarding rice production byproducts and the efficiency of wastewater purification systems.

Here, RH and RHA particles are incorporated into PA6/GO nanocomposite systems, and the performances of fabricated sustainable nanocomposites are studied. Moreover, to investigate the role of surface modification, RH and RHA particles are functionalized with a silane agent. The solution-casting technique, using formic acid as the solvent, is employed for fabricating samples, as formic acid is the most common solvent for the fabrication of PA6-based fibers. Silane-functionalized-RHA particles used for preparing nanocomposites are in nano dimensions. In addition, GO nanosheets are perfectly exfoliated in the structure of the functionalized-RHA/GO/PA6 nanocomposite. Therefore, this nanocomposite system performs the most enhanced properties.

2. Materials and methods

2.1. Materials

PA6 (GH011-1, density: 1.12–1.14 g/cm^3) was purchased from Tisan Engineering Plastics (Turkey). RH particles were obtained from a local rice mill in Fars Province, Iran, and washed several times with deionized water and sun-dried prior to use. Graphite powder used in this study was from LECO Co (USA). Sulfuric acid (98%, H_2SO_4), potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) were purchased from Merck (Germany), and used as received. 3-Aminopropyl-triethoxysilane was purchased from Sigma-Aldrich (USA). Hydrogen chloride (HCl), acetone, ethanol and formic acid were all obtained from Dr. Mojallali Chemicals (Iran).

2.2. Preparation of GO

GO suspension was prepared according to the procedure described in the literature [25,26]. In a typical procedure, 1 g of graphite powder was put in a round-bottom flask and 100 mL of H_2SO_4 was added to the flask. The mixture was stirred for about 15 min and then, 6 g of $KMnO_4$ was gradually added to the flask. The mixture was then stirred for about 2 h and then the temperature of the mixture was raised to 35 °C. The mixture was kept at this temperature for about 4 h; through that oxidation reaction took place. Afterward, 300 mL of distilled water was poured into the reaction mixture, and then the mixture was allowed to stir for 15 more min. To terminate the oxidation reaction, 50 mL of H_2O_2 aqueous solution (15%) was added to the mixture to reach a yellow–brown graphite oxide mixture. The prepared graphite oxide mixture was first washed for five times with a 10% HCl solution and then, five