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Application of ultrasonic irradiation as a benign method for production of glycerol plasticized-starch/ascorbic acid functionalized MWCNTs nanocomposites: Investigation of methylene blue adsorption and electrical properties

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ABSTRACT

A solution mixing and ultrasonic dispersion method as a green, the fast, inexpensive and effective technique was utilized to prepare glycerol plasticized-starch (GPS)/ascorbic acid (AA)-MWCNTs nanocomposites (NCs) via the introduction of various amounts of AA-MWCNTs (3, 6 and 9 wt%) as filler into GPS matrix. The GPS was synthesized by addition of glycerol (50%) as a plasticizer to starch which enhances its flexibility. Characterization of the obtained GPS/AA-MWCNTs NCs was accomplished by different techniques. The optimum filler content for the generation of fine electrical conductivity and good mechanical properties was found to be about 3 wt%. The distribution of AA-MWCNTs at the low content (3 wt%) in the GPS matrix was better due to the strong linkage between nanofiller and GPS in GPS/AA-MWCNTs NC. The results of adsorption studies showed that the fabricated NC can be a good adsorbent for removal of methylene blue (MB) dye from aqueous solutions.

1. Introduction

The synthetic polymers are human-made materials which derived from petroleum oil. Most of these petro-based polymers could not be degraded and are one of the most sources of solid wastes. Also, petroleum resources are limited and fast depleting. These problems can be addressed by using biopolymers obtained from biomass sources which are renewable, environmentally friendly and biodegradable. These polymers decompose easily into carbon dioxide, water, methane, inorganic compounds and biomass via microbial activities [1,2]. Among all the biopolymers, starch is one of the leading candidates because of its availability, renewability, good biodegradability, high performance and low price [3,4]. It is a semicrystalline polymer accumulated in granules as a reserve in the majority of plants. This polymer consists of two polysaccharides: amylose and amylopectin. The amylose is an almost linear molecule with an extended helical twist in which the repeating units are bonded by α (1 − 4) linkages whereas amylopectin, have the same backbone structure as amylose but with many α-1,6 glucosidic branching points. The properties of starch depend mainly on the ratio of these two constituents and the relative contents of amylose and amylopectin depend upon the plant source. Corn starch granules have about 70% amylopectin and 30% amylose [5,6]. However, pure starch is brittle because of strong interactions between starch macromolecules and not usable as a film. This polymer must be plasticized for ease of processing. Thermoplastic starch (TPS) or plasticized starch (PS) is a material that is attained by the destruction of the starch granules structure in the presence of plasticizers, for example, sorbitol, sugars, water, glycerol, formamide and other non-volatile materials with low molecular weight that can form hydrogen bonds with starch. Plasticizers make the pure starch plastic because these molecules disrupt inner H-bonds of starch and reduce starch–starch interactions because these interactions are replaced by starch–plasticizer adhesions [7,8].

Wang et al. fabricated PS using various amounts of urea. They showed that PS films having urea amount of 10–30%, the tensile strength of the TPS was reduced, and the elongation at break was enhanced [9]. Qiao et al. reported plasticization of the corn starch via a mixture of maltitol, sorbitol, and xylitol which decreased the humidity sensitivity and enhanced the mechanical properties and thermal stability of the obtained films [3]. Zhang et al. investigated the influence of the glycerol and ionic liquid 1-ethyl-3-methylimidazolium-acetate ([Emim][OAc]) on the properties of starch [10]. Unfortunately, TPS is a moisture sensitive material, demonstrating poor mechanical properties

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and thermal stability. Loading with nanofillers to fabricate nanocomposites (NCs) has become one of the more promising routes to overcome these limitations [11]. Heydari et al. incorporated Na-Montmorillonite (Na–MMT) into glycerol plasticized-starch (GPS) which improved the physical properties of corn starch films [4]. Qian et al. prepared GPS/carbon black-oxide (CBO) NCs via the introduction of CBO into GPS matrix. The presence of CBO enhanced water vapor resistance, thermal stability and mechanical properties of GPS [11]. Ma et al. reported that homogeneous distribution of graphene oxide (GO)/reduced graphene oxide (RGO) filler in the PS matrix enhanced the humidity barrier and mechanical properties [12]. Cheng et al. produced PS/carbon nanotube (CNT), PS/CNT oxide (OCNT) and PS/reduced CNT (RCNT) NCs. CNT, OCNT, and RCNT enhanced the electrical conductivity, mechanical properties, and humidity resistance of obtained NCs [13]. Carbon is capable of forming many allotropes such as fullerenes, carbon nanotubes (CNTs), carbon black, and graphene because of its valency. Nowadays, carbon allotropes-based NCs have attracted significant research interest due to their unique bonding properties and vast applications. For example, the graphene based NC could be a potential candidate for several biomedical applications as cost effective aspects in sensing, in vitro and in vivo evaluation, scaffolds for the tissue engineering as biomaterials [14–18]. Multi-walled carbon nanotubes (MWCNTs) are another allotrope of carbon which has received increasing attention due to their exotic properties for instance high mechanical strength, large surface areas and aspect ratios as well as their high thermal and electrical conductivities. The combination of these properties suggests that MWCNTs can act as potential filler in high-performance polymer composites [19–22]. However, without surface modifications, CNTs will aggregate in polymer matrix due to van der Waals and electrostatic forces between the carbon surfaces and give poor reinforcing effects [23]. A useful approach to prevent nanotube aggregations is a functional modification of CNTs which helps to attain better distribution and stabilization of CNTs within a polymer matrix [24]. One of the most useful materials which utilized for surface modification of MWCNTs is ascorbic acid (AA) (vitamin C). This eco-friendly and bio-safe compound enhances the interfacial interaction and compatibility between AA-MWCNTs and polymeric matrix thus CNTs don't form aggregates and uniformly disperse into polymer [25–27]. Recently, CNTs/TPS NCs have been researched to unite the remarkable properties of CNTs and TPS [7,9,13,28–30].

Ultrasound is the process of propagation of the compression waves with frequencies at and above 20 kHz which produce changes through wave propagation. When an ultrasonic wave is passed through a liquid, the acoustic cavitation effect occurred which involves the formation, growth, and collapse of bubbles in the liquid. The bubble collapse induces extreme transient conditions, for example, micro-streaming, local extremely high temperature and pressure, mechanical agitation that allows the reaction to proceed instantaneously. Thus, this process is valuable, due to the elimination of high temperature, pressure and long reaction time as well as laborious reaction steps. By using this method, the agglomerates of particles in the suspension reduced considerably. When applied on liquid, ultrasonic irradiations induce pressure waves that produce cavities. At low pressure, the size of the cavities oscillates around a constant value and bubbles develop and burst at the surface of the liquid. At high pressure, high-intensity ultrasonic waves generate, enlarge and collapse a lot of bubbles in the liquid solution. The size of the cavities oscillates around an increasing value, and then strong stress is produced by cavities collapse. This induced stress breaks down agglomerates into smaller aggregates. Thus, this technique can be utilized in the homogenization process and reduction the particle size and activate them. Therefore we utilized an ultrasound assisted method for the fabrication of NCs [31–33].

Different polymer/CNT NCs were utilized in order to removal of methylene blue (MB) from the wastewater. Sui et al. reported an efficient removal of methyl orange (MO) and MB from aqueous solutions by calcium alginate (CA)/MWCNTs NCs [34]. Sun et al. demonstrated that the hemicellulose-g-poly (methacrylic acid)/MWCNTs NCs hydrogel can efficiently remove methylene blue from aqueous solutions [35]. Inyang et al. fabricated hybridized CNT–biochar NCs as an efficient and cheap sorbent for the elimination of MB from the wastewater [36]. Jing et al. synthesized a new superabsorbent based on MWCNTs–xylan composite and poly (methacrylic acid) (PMAA) with high adsorption capacity and removal rate of MB [37]. MWCNT-starch-iron oxide was employed to eliminate MO and MB from the wastewater by Chang et al. [38]. In our previous work, the removal of MO from aqueous solutions using starch/AA-MWCNTs NCs was investigated. It was found that starch is an outstanding superabsorbent owing to its hydrophilic hydroxyl groups and outstanding properties (as cited above). In fact, homogenous distribution of starch/AA-MWCNTs NCs in water occurred in order to obtain a hydrophilic soluble mixture. This occurrence improved contact surface between modified nanofiller and dye molecules and reduced the aggregation of MWCNTs which make the diffusion of dye molecules to the surface of nanofiller feasible [39]. These good results encouraged us to evaluate the efficiency of starch/CNTs NCs for removal of MB from the wastewater. In this present study, plasticization of corn starch using glycerol was carried out with the aim of enhancing the mechanical properties and decrease the moisture sensitivity of starch and GPS/AA-MWCNTs NCs were prepared in order to improve the hydrophilicity and biocompatibility of MWCNTs via solution mixing and ultrasonic dispersion technique. Different ratios of AA-MWCNTs were incorporated into GPS under ultrasonic irradiation conditions as a low-cost green technique and the effects of plasticization and MWCNTs percentage on the structure and properties of the obtained NCs were investigated by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), UV–visible (UV/vis) spectroscopy, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The main purpose of this work was evaluating the potential use of GPS/AA-MWCNTs NCs as an adsorbent for the removal of MB from the wastewater and influence of AA-MWCNTs reinforcement on the electrical conductivity of these NCs. The obvious advantage of this work is the utilization of starch as a polymeric matrix which has several advantages and AA (as eco-friendly and bio-safe material) for surface modification of MWCNTs. Also, GPS/AA-MWCNTs NCs are biocompatible and biodegradable adsorbent. An advantage of other adsorbents is their reusability.

2. Materials and methods

The carboxylic acid-functionalized MWCNTs (CA-MWCNT; carboxyl content 2.00 wt% and a purity > 95 wt%) used in this study were purchased from Neutrino Co. (Iran). The outer diameter of CA-MWCNT was 10–20 nm, and it has an inner diameter of 5–10 nm with a length of about ~30 μm. Vitamin C was obtained from Merck Chemical Co. (Germany). N, N-dimethylacetamide (DMAc) (d = 0.94 g cm^{-3} at 20 °C) was used as received without further purification and obtained from Merck Chemical Co. (Germany). Corn starch (Formula Weight: $(162.15)_n$, Formula: $(C_6H_{10}O_5)_n$, Density (g/mL): 1.45–1.6,) was purchased from SK-Science kit (Tonawanda NY, 14150, USA, with the product code of 81460-03). The corn starch was composed of 25% amylose and 75% amylopectin. Glycerol was purchased from Tianjin Chemical Reagent Factory. MB ($C_{16}H_{18}ClN_3S$, molecular weight 319.85 g.mol^{-1}) was obtained from Merck Chemical Co (Fig. 1).

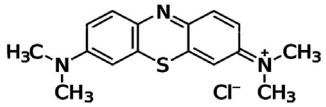

Fig. 1. Structure of MB.