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The influence of bovine serum albumin-modified silica on the physicochemical properties of poly(vinyl alcohol) nanocomposites synthesized by ultrasonication technique

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ABSTRACT

In this study, for the first time polymeric nanocomposite (NC) films of poly(vinyl alcohol)/SiO_2@bovine serum albumin (PVA/SiO_2@BSA) were synthesized by solution casting method under facile and fast method of sonication. In this regard, SiO_2 nanoparticles (NPs) were modified by BSA, at room temperature by using phosphate buffer and ultrasonic-assisted method. Then, PVA/SiO_2@BSA NCs were prepared by insertion of variant amount (3, 6 and 9 wt%) of SiO_2@BSA into the PVA matrix, under ultrasonic irradiation. The morphological traits of the NCs were surveyed by Fourier transform infrared spectroscopy, transmission electron microscopy, X-ray diffraction and field emission scanning electron microscopy. It was detected that NPs incorporation didn't remarkably affect the crystallinity and morphology of the NCs. TEM images indicated that the inserted NPs have good diffusions in the PVA matrix, and their embedment in the matrix significantly upgraded its thermal, optical and mechanical behaviors. The tensile strength showed more than 2-fold increase and the thermal stability exhibited about 37% enhancement that was higher, in comparison with those of the similar NCs. This showed that the prepared NCs can have potential application in food packaging.***

1. Introduction

To date, SiO_2 nanoparticles (SNPs) are broadly used in chemical sensors [1], photonic crystals [2], nanofillers for nanocomposite (NC) materials [3], biosensors [4], catalysts [5], quantum dots [6], and in producing chemical containers and optical fibers [7]. Their chemical reactivity and unique traits are correlated with their uniform particle size, great surface area, well biocompatibility and stability, low toxicity, low price [8], supreme insulation and bad thermal conductivity [9]. For instance, Shang et al. [10] showed that the stability of cytochrome adsorbed on the SNPs enhances with reducing the particles size from 35 to 4 nm. Apart from the mentioned advantages, the SNPs possess high steric hindrance, low electron transfer capability and low electrocatalytic activity [8].

Polymer NCs have drawn excessive attention owing to the enhanced traits with the insertion of less amount of nanoparticles (NPs), compared to the common composite systems [11,12]. The loading of the low deal of NPs remarkably ameliorate the matrix behaviors, and in several cases, it prompts to an inimitable collection of properties [13–17].

Polymeric NCs are extensively being used in numerous fields for example flexible optical fibers [18], energy storage [19] and optical and magnetic storage systems [20]. This could be by reason of their low weight, high elasticity, low preparation temperature and low price [21–23]. Among different polymers, poly(vinyl alcohol) (PVA) has a semi-crystalline [24], environmentally friendly nature that can be exploited as the matrix owing to the film forming ability [25], good mechanical, thermal and chemical stability [26,27], non-toxicity and biocompatibility [28,29]. As a result of the rich hydroxyl functional groups, it has a strong tendency to absorb water and it can be also dissolved in water without excessive heating [30]. Therefore, the PVA-based NCs usually lack mechanical stability and strength in aqueous solutions [31]. There are several ways to conquer this problem; (a) cross-linking modification by different cross-linking agents, such as glutaraldehyde [32], fumaric acid [33] and amic acid [34] and (b) fabricating hybrid material through incorporation of inorganic nanofillers into the polymeric matrices including carbon nanotubes [35], activated carbons [36], zeolite [37] and metal oxide NPs. In the first approach, the selectivity of the cross-linked matrix can be efficiently ameliorated, whereas the permeate flux reduces sharply. For the last

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approach, unique advantages of the inorganic nanofillers such as high chemical and thermal stability combine with good processability and low cost of the matrices. Therefore, the applications of NCs are largely restricted by the incompatibility of the NPs with polymeric phases, thus a performance failure [31,38]. Conversely, the NPs tend to agglomeration, because of the great surface energy [39]. Therefore, surface treatment of NPs with surface active organic molecules not only declines their agglomerations but also increases their compatibility with the polymer matrices [40].

Albumin is considered as a protein gained from a diversity of origins, such as bovine serum albumin (BSA), human serum albumin and egg white. It makes up the main member of solvable proteins of a circulating system that allows preserving osmotic pressure, connection, and transportation of nutrients to cellulose. Albumin possesses variant privileges for instance biocompatibility, biodegradability, heat resistance up to 60 °C for 10 h, stability in pH range of 4–9 and high solubility at pH of 7.4 [41]. These traits merged with non-toxicity and good ligand-connection trait [42] which made it as an eligible biosafe modifier for modification of the NPs. In 2015, Joseph et al. [43] have coated magnetic NPs by BSA that the size of NPs was incremented. They expressed that the coating of NPs by BSA was occurred by corona formation. Zhai et al. [44] have modified the SiO_2 spheres with BSA using a Schiff base technique, which included chemical binding of aminopropyl groups with the hydroxyl group of the SNPs, chemical insertion of glutaraldehyde and chemical linking of BSA, respectively. Wu et al. [45] fabricated mesoporous PVA functionalized with thiol groups to graft to the SiO_2 to achieve appropriate composites to omit Cu^{2+} from its aqueous solution. Li et al. [46] used inorganic SiO_2 sol to modify the organic PVA via an in-situ sol–gel method that significantly affects mechanical traits of the PVA. Peng et al. [47] synthesized PVA/SNP NCs by solution combining and self-assembly route, in which SNPs have acted as a template. Mallakpour et al. [48] have manufactured PVA-based NCs containing SNPs modified with ascorbic acid and citric acid (PVA/SiO_2@AA-CA) via solution casting method and ultrasound waves. They also investigated variant characters of the NCs that will be compared with the existing study. In another study [49], the SNPs surface was modified with biosafe vitamin B_1 through the same method and then the modified SNPs with 3, 5 and 7 wt% were applied for reinforcing the PVA matrix. The prepared NCs were referred as PVA/SiO_2@VB_1 NCs that their properties significantly improved by embedment of the modified SNPs. Similarly, Mallakpour research group [50] employed N-trimellitylimido-l-methionine for surface modification of the SNPs and used the prepared NPs as a filler for the poly(amide-imide) matrix. Finally, the fabricated NC was used for improving properties of the PVA matrix referred as PVA/SiO_2@PAI.

Ultrasonic technology, as one of the recent systems, has been engrossed more regards in last years. This method is superior to usual chemical methods in phrases of equipment enterprise or convenient ability. The ultrasonic method has been declared to be a benign and energy impressive method for processing the reactions [51,52].

The ultrasonic process doesn't require heat generator and it applies the ultrasonic irradiation having high frequency that leads to producing the NPs with uniform size [53]. Thus, this procedure has been employed for turning, milling, tube indentation, welding and powder metallurgy [54]. This technique proceeds through droplet formation and can be understood by two theories: cavitation theory and capillary wave notion. In the first theory, with irradiating the liquid phase microbubbles or cavities are generated. The cavities are frequently protected and struck by ultrasonic waves and finally collapse that produce high temperature and pressure. Therefore, fine droplets can be shaped and the moderate condition for the reactions can be provided. In the last theory, the vibrations on the liquid surfaces created via high-frequency ultrasonics that is unstable and atomic. This theory suggests that mist formation happens when unstable vibrations disconnect the capillary waves far from the bulk fluid. Thus, the glob extent of the produced mist relies on the capillary wave wavelength. With gaining the wave frequency, the wavelength of the capillary decreases [55–57]. The tiny hotspots of the ultrasonic system provide enough energy for some significant chemical and mechanical effects. The recent major areas for sonochemistry research and its development include synthesis, electrochemistry, environmental protection, food technology, materials and therapy. Acoustic cavitation can supply fast and clean syntheses systems that linked well with what so-called Green Chemistry. In addition, sonoelectrochemistry could be applied for remediation and pollutant degradation, and to offer efficient sensors for recognition of different species in water and in atmosphere [58].

In this paper, the surface of silica NPs was covered by biocompatible molecules, BSA, under ultrasound irradiations. Treated NPs (SiO_2@BSA) were characterized by diverse techniques. In the next step, PVA-based NC films were synthesized by insertion of the SiO_2@BSA NPs with variant weight percentages (3, 6 and 9 wt%) that led to the formation of the PVA/SiO_2@BSA NCs with improved properties, including UV–Vis absorption, water contact angle, thermal and mechanical properties.

2. Experimental

2.1. Material

SiO_2 nano-powders were supplied from Neutrino Co. (Tehran, Iran) with average particle size of 10–15 nm. PVA with Mw = 145,000 g/mol and BSA with Mw = 66.463 Da were purchased from Merck Chemical Co. (Germany) and Sigma Aldrich (Germany), respectively.

2.2. Characterization techniques

The modification and fabrication processes were accomplished under ultrasound irradiation using TOPSONICS ultrasonic liquid processor (Tehran, Iran) with a wave of frequency 20 ± 1 kHz and power of 100 W. For applying the ultrasonic waves, the ultrasonic horn was plunged directly in the reaction vessel. During reaction, the ultrasound power of 100 W and frequency of 25 kHz were chosen as optimum condition to distribution of NPs. At least 10–15 mL of the solvent in a narrow vial is required to completely immersing the ultrasound probe. Since the heat resistance of BSA is 60 °C, the reaction vials were placed in an ice bath to prevent the heat increasing and then ultrasonicated for 7 min. The ultrasonication produces high temperature and high pressure that facilitates breaking of the former interactions and creating of the new interactions. Fourier transform infrared (FT-IR) spectra were noted using KBr pellets between 400 and 4000 cm^{-1} on a Jasco 680 spectrophotometer (Jasco, Japan) with a resolution of 4 cm^{-1}, at room temperature (RT). X-ray diffraction (XRD) patterns were attained using a Philips X-pert MPD diffractometer (Santa Barbara, California, USA) by Cu Kα (λ = 1.5418 Å) in the range of 10–80° and speed of 0.5 °/min. The patterns analysis was performed by "X'Pert HighScore" software. Morphology of the NCs and NPs were surveyed by field emission scanning electron microscope (FE-SEM) [HITACHI (S-4160)]. NPs dispersion and sizes were studied using a transmission electron microscope [TEM, Philips (CM 120)] with a voltage 150 kV. TEM image analysis was accomplished by Digimizer 4.1.1.0 software. Mechanical traits of the samples were considered by Testometric Universal Testing Machine M350/500 (UK) at a speed of 25 mm/min at RT. The dimension of samples was 40 × 20 × 0.6 mm^3. The results were the average of two test runs. Ultraviolet–visible (UV–Vis) absorptions were recorded using a Jasco V-570 spectrophotometer. Thermogravimetric analysis (TGA) was investigated using a STA503 TA instrument in the range of 100–800 °C at a speed of 20 °C/min under argon atmosphere. The Brunauere-Emmette-Teller (BET) analysis for determination of surface area of the NPs and NCs was performed by a NANOSORD (Iran). The energy dispersive X-ray spectroscopy (EDX) was measured via a SERON Al52300 spectrometer.