Ultrasonics - Sonochemistry 41 (2018) 27–36

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

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

Microwave and ultrasound-assisted synthesis of poly(vinyl chloride)/riboflavin modified MWCNTs: Examination of thermal, mechanical and morphology properties

Amir Abdolmaleki[a,b,c,*], Shadpour Mallakpour[a,b,c,*], Faezeh Azimi[c]

[a] Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran
[b] Research Institute for Nanotechnology and Advanced Materials, Isfahan University of Technology, Isfahan 84156–83111, Islamic Republic of Iran
[c] College of Pardis, Chemistry Section, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran

ARTICLE INFO

Keywords:
Ultrasonication
Multi-walled carbon nanotube
Riboflavin
Poly(vinyl chloride)
Nanocomposites
TEM

ABSTRACT

This study focused on the preparation and investigation of physicochemical features of new poly(vinyl chloride) (PVC) nanocomposites (NCs) including different amounts of carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) functionalized with riboflavin (RIB). Firstly, to increase the hydrophilicity of MWCNTs, the surface of them was functionalized by incorporating and formation of ester groups with RIB as a low cost and environmentally friendly biomolecule through ultrasound and microwave irradiations. Afterwards, PVC/RIB-MWCNTs NCs were fabricated via the solution casting and ultrasonic dispersion methods. Prepared NCs were examined by X-ray diffraction, thermogravimetric analysis, field emission scanning electron microscopy, transmission electron micrograph, and Raman spectroscopy. The PVC/RIB-MWCNTs NCs (12 wt%) showed the higher mechanical and thermal behavior as compared to other concentration of MWCNTs.

1. Introduction

Polymeric nanocomposites (NCs) consist of a polymer having nanofillers dispersed in the polymer matrix. NCs have been focus of many researchers world-wide due to their extensive utilization for chemical, mechanical, and optical industries. These materials can be extensively applied in various usages, including gas sensors, coatings, pharmaceutics, drug delivery, medical, adhesion and constancy of colloidal distributions [1–3].

Among polymers, poly(vinyl chloride) (PVC) is a cheap commodity plastic material that used in numerous types of industrial and domestic applications such as a membrane, packaging, sheets, pipes, wire, medical and cable insulations [4] and has film forming ability. The PVC has some intrinsic disadvantages, such as low thermal performance and high brittleness. So, to enhanced these confines and attain favorite performance, nanofillers should be homogeneously disseminated in the polymer matrix [5,6].

Among various reinforcing nanoscale components, clay [7], multi-walled carbon nanotubes (MWCNTs) [8], silicon dioxide [9], and titanium dioxide [10] are the most mutual nanofillers employed in the over the past two decades to create an extraordinary efficiency of NC materials. The MWCNTs are presently considered as reinforcing fillers for polymeric NCs owing to their exceptional structural, mechanical and, electrical behaviors [11–13]. A blend of CNTs with polymers is powerfully influenced by the uniform distribution of CNTs in the polymeric composites. The CNTs frequently accumulate owing to the van der Waals contacts that confine their possible usage in different applications. For this cause, a number of researches have concentrated on CNTs treatment and homogenous dispersion of them. Functionalization of CNTs is usually done by surface oxidation, grafting of hydrophilic functional groups, and the surface modification of nanotubes based on surfactants, long polymer chains [14–18] and also biomolecules such as vitamins, amino acids, carbohydrates, proteins, and nucleic acids [19–23]. Therefore, development of simple and cost-effective chemical methods for covalent functionalization of CNTs has become an important area of research both from fundamental and application standpoints.

Ultrasound and microwave irradiation are increasingly valuable tools in organic chemistry, since it offers a versatile and facile pathway for a large variety of syntheses. Without doubt, compared with conventional thermal heating, ultrasound and microwave irradiation have some important advantages: substantial decrease of reaction time,

* Corresponding authors at: Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Islamic Republic of Iran.
E-mail addresses: abdolmaleki@cc.iut.ac.ir, amirabdolmaleki@yahoo.com (A. Abdolmaleki), mallak@cc.iut.ac.ir, mallak777@yahoo.com, mallakpour84@alumni.ufl.edu (S. Mallakpour).

http://dx.doi.org/10.1016/j.ultsonch.2017.09.018
Received 2 August 2017; Received in revised form 8 September 2017; Accepted 10 September 2017
Available online 11 September 2017
1350-4177/

environmentally friendly reactions (using small amounts of solvents or being "solvent free" reactions and generating fewer side products), and, in many cases, improved yields and high purity of the compounds, increased selectivity, lower costs and simplicity in handling and processing [24]. In a range of plans available to avoid aggregation of CNTs in polymer matrix, ultrasonic irradiation based technique could be employed as an effective one to functionalize the CNTs surface via coupling agents and increase their compatibility and interaction with polymer matrix [25,26]. Ultrasound is a sound wave with frequency above 20 kHz. Acoustic cavitation and acoustic streaming are the two basic phenomena associated with any ultrasonic process. Ultrasonic waves consist of compression and expansion cycles. When an ultrasonic wave is passed through a liquid, a positive pressure is exerted on the liquid during the compression cycle and a negative pressure is exerted during expansion cycle. During this negative pressure, molecules are pulled away from each other. This results in formation of cavities in liquid. Over many cycles, these cavities grow and enlarge. Finally, implosion of the cavities occurs, creating temperatures of the order of 5000 K and pressures of 500 atmospheres [27–29]. The energy released from acoustic cavitation phenomenon, can accelerate the chemical reactions, initiate new reactions that are difficult to achieve under normal conditions, and lead to formation of homogeneous NCs with a good dispersion and improved properties. Microwave irradiation is composed of an electric and magnetic field, and can cause high frequency motion and rotation of dipoles. It can rapidly transfer energy directly to the reactants, and causes an internal and external temperature rise almost at the same time, in contrast with conventional conductive heating. This allows rapid decomposition of the precursors, thus creating highly supersaturated solutions where nucleation and growth can take place to produce the desired nanocrystalline products [30,31]. Since microwave and ultrasound have different irradiation mechanisms and functions, the combination of these two types of irradiation and its application in chemical synthesis appears very interesting [32].

Mallakpour et al. prepared NCs containing starch reinforced with bioactive ascorbic acid functionalized MWCNTs via the solution casting under ultrasonic irradiations. They showed which prepared NCs can be as a good adsorbent for the removal of methylene blue dye from aqueous solution [33]. In other work, in order to prepare NCs based on the technique reported, they selected poly(N-vinyl-2-pyrrolidone) as a biocompatible polymer matrix and treated copper (II) with citric acid and ascorbic acid as a nanofiller. The fabricated NCs showed an improved thermal stability in comparison with the neat polymer. Also, according to UV absorption spectra, it is clear which fabricated NCs can be utilized in UV protecting applications [25]. Riboflavin (RIB), also known as vitamin B_2, is a yellow substance with molecular formula $C_{17}H_{20}N_4O_6$ that includes a conjugated isoalloxazine ring (flavin) and a five-carbon carbohydrate (ribitol). According to interesting biomedical applications of PVC such as healing devices, and orthopedic surgeons, RIB as a biological and bio-safe compound, enhances the interfacial interaction and compatibility between nanotubes and PVC matrix for preparation of NCs with better thermal and mechanical properties [34,35].

The main focus of this study is surface treatment of MWCNTs through ultrasonic irradiation and microwave-assisted process, production and investigation of PVC/RIB-MWCNTs NCs via ultrasonic irradiation alone and discussion about their morphology mechanical, thermal and properties.

2. Experimental

2.1. Materials

PVC with molecular weight 78,000 g mol^{-1} and tetrahydrofuran (THF) and *N,N*-dimethylacetamide (DMAc) (d = 0.94 g cm^{-3} at 20 °C) were supplied from the LG Chem (Korea), Jeong Wang (Korea), and Merck Chemical Co. (Germany), respectively. MWCNTs (outer diameter of 10–20 nm, inner diameter of 5–10 nm, and length ~30 μm) with high purity and carboxyl content of 2.00 wt% were purchased from Neutrino Co. (Iran). RIB ($C_{17}H_{20}N_4O_6$ MW: 376.36) was obtained from ACROS.

2.2. Characterization

The chemical structure of the materials was recorded on a FT-IR (JASCO-680) instrument in the region of 4000–400 cm^{-1}. Raman spectra of samples were obtained in the range of 1000–2000 cm^{-1} using Teksan (Tekram P50C0R10) Raman spectrometer. Thermoanalytical investigations of samples were carried out in argon flow through a TGA system (STA503 TA) at a heating rate of 20 °C min^{-1} from 25 to 800 °C. The crystal structures of films were identified using Philips X'PERT MPD (Germany) XRD instrument with Cu Kα radiation of λ = 0.154056 nm in the scanning range 2θ = 10–80°. The mechanical testing was conducted using the Testometric Universal Testing Machine M350/500 (UK) at a rate of 0.5 mm min^{-1} at 25 °C. Morphology of samples, distribution and size of nanotubes in the PVC matrix were recorded via field emission scanning electron microscopy (FE-SEM) model HITACHI (S-460) and transmission electron microscopy (TEM) model Philips (CM 120, Netherlands). Experiments were carried out by ultrasonic liquid processor model TOPSONIC (100 W, 20 kHz) (Tehran, Iran).

2.3. Modification of MWCNTs with RIB

First, RIB (100 mg) was mixed with DMAc (25 mL) at 60 °C. Prepared solution was reacted with MWCNTs-COOH (50 mg) and concentrated HCl (0.1 mL) by continuous stirring for 24 h at 80 °C. After that, the suspension was heated under microwave irradiation to 120 °C and power of 700 W for 15 min. The obtained suspension was sonicated by TOPSONIC homogenizer ultrasonic liquid processor (Tehran, I. R. Iran, frequency of 20 kHz and power of 100 W), for 1 h (20 kHz frequency and 80 W power). Finally, the resulted precipitate was centrifuged, washed with distilled water and dried at ambient temperature [36].

2.4. Fabrication of PVC/RIB-MWCNTs NCs

PVC (0.1 g) was dissolved in THF (10 mL) and stirred at ambient temperature for 30 min. Then, different quantities of the RIB-CNTs (4, 8 and 12 wt%) were added to the dissolved PVC. The suspension was stirred for one day and sonicated with the power of 80 W for 1 h. At the end, the solution was cast into petri dish and dried at 25 °C for fabrication of PVC/RIB-MWCNTs NC films. The dispersion of RIB-MWCNTs within the PVC matrix was carried out with several ultrasonic powers (20, 40, and 80 W) and the optimum power to achieve a good distribution of RIB-MWCNTs for the fabrication of PVC/ RIB-MWCNTs NCs was found to be 80 W.

3. Results and discussion

3.1. PVC NC films preparation

The MWCNTs owing to their excellent thermal resistance, mechanical and optical behaviors, are known as an impressive reinforcement in preparation of polymer NCs via enhancing interfacial interaction between PVC matrix and MWCNTs. In order to create a uniform surface as well as to prevent the agglomeration of the MWCNTs, surface modification was executed. This procedure improves surface charge, surface energy, roughness, hydrophilicity, and reactivity [37,38]. Ultrasound is utilized to control size dispersion and advancement of the nanofillers distribution in the macromolecules and finally create distributed phases. The ultrasonic method with acoustic cavitation creates high localized pressures and temperatures which are from the effect of