Progress in Organic Coatings 121 (2018) 120–129

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

An ultrasonic assisted process for the synthesis of poly(vinyl alcohol)-poly (*N*-vinyl-2-pyrrolidone) nanocomposites filled with modified nano-Zirconia

Shadpour Mallakpour[a,b,*], Elaheh Shafiee[a]

[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*

ARTICLE INFO

Keywords:
Poly(vinyl alcohol)
Poly(*N*-vinyl-2-pyrrolidone)
Modified ZrO_2 nanoparticles
Ultrasound irradiation
Thermal resistance
Water contact angle

ABSTRACT

Equal weight ratio of PVA/PVP blends solutions filled with several amounts of modified Zirconia (ZrO_2) nanoparticles (NPs) via thiamine (Th) up to 7 wt% were prepared under ultrasound irradiation with casting/solvent evaporation method in the form of films. Existence of functional groups in the coating layer structure associated with the samples was confirmed by Fourier transform infrared spectroscopy analysis. Ultraviolet-visible absorption was enhanced by employing of ZrO_2 NPs as effectual filler in NCs. Microscopic observations revealed that NPs have proper compatibility with the PVA and PVP matrices and uniformly dispersed into the their matrices. The reduction in contact angle was observed with increasing the amount of ZrO_2-Th. Thermal gravimetric analysis results showed that the thermal resistance of NCs was higher than the pristine PVA-PVP blend. Finally, antibacterial test results showed that all the NCs don't show any antibacterial activity. Due to the presence of PVA and PVP in the NCs, they could be biocompatible as well as biodegradable.

1. Introduction

The macromolecule modification by mixing two or more distinct polymers to obtain compounds with improved properties, arises an increasing interest reflected by the big number of publications [1]. Polymer blends are a physical combination of structurally various homopolymer or copolymers that interact through secondary forces [2]. Miscibility in polymeric blends is assigned to special interactions such as hydrogen bonding between polymeric components [3].

Polymeric blends are prepared by various procedure and amongst them solution blending is very simple and fast because it requires easy tools and not involved any complicated process [4]. The films formed by to combine of polymers repeatedly result in modified physical and mechanical features compared to films made from an individual ingredient [5]. Mondal et al. prepared blend NCs PVA/PVP/sodium montmorillonite by sonication and investigated the effect of PVP on the morphology and physical properties of PVA/sodium montmorillonite NC films. Inclusion of PVP in PVA/sodium montmorillonite matrix enhances the hydrogen bonding interactions between PVA and sodium montmorillonite and thus increases the mechanical properties and thermal stability of the PVA/PVP/sodium montmorillonite NC [6].

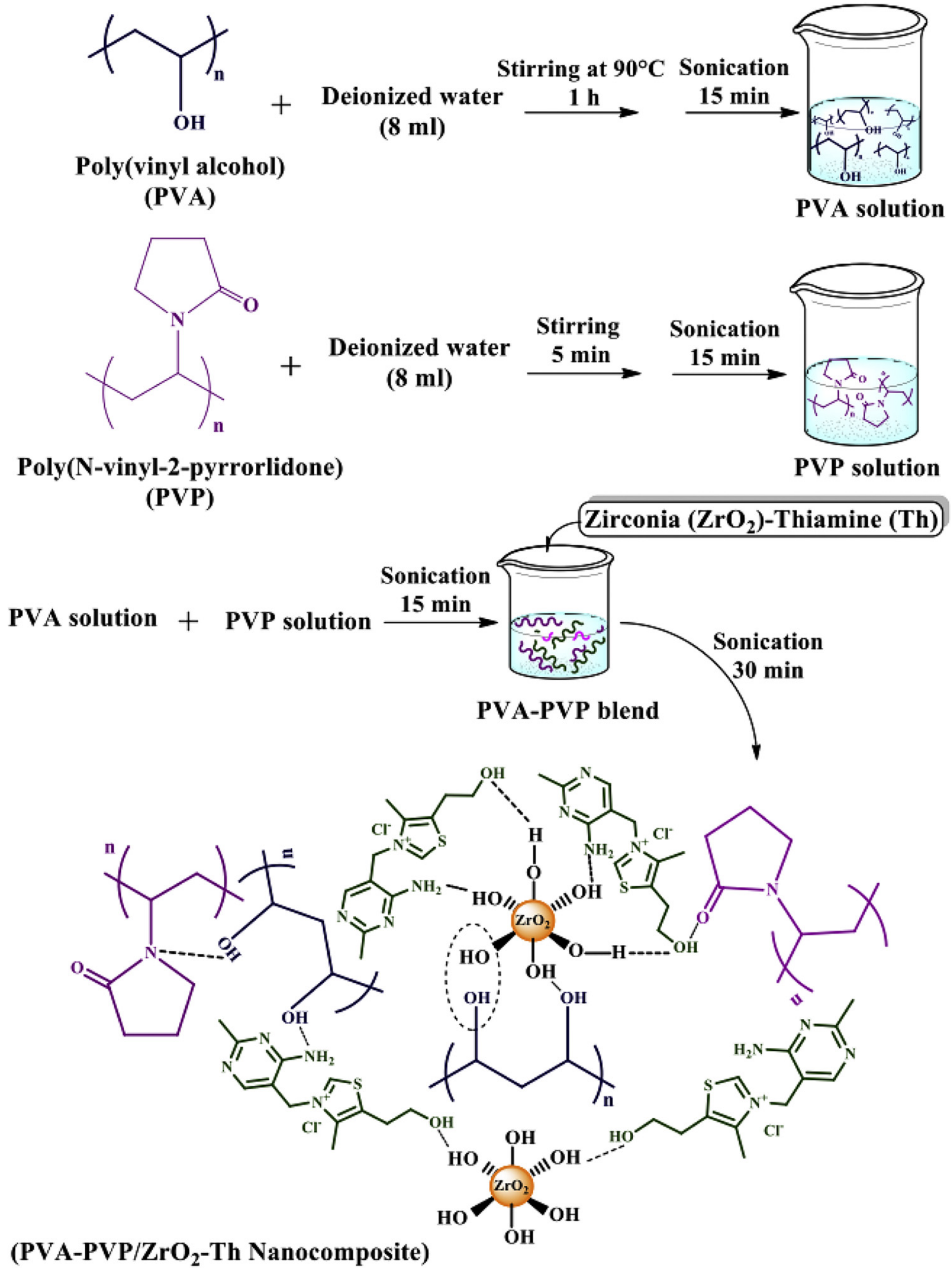
Poly(vinyl alcohol) (PVA) is a synthetic polymer, biocompatible, odorless, nontoxic and noncarcinogenic with good film forming capability and high hydrophilic properties. PVA has been broadly used for the preparation of mixtures and composites [1,7–11].

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a combinatorial polymer that has a well-defined structure via a carbon backbone and pyrrolidin side group [12]. This polymer has fine biocompatibility and low toxicity demeanor and can be used in plenty technical applications due to its excellent physiological adaptability [4,13,14]. Indeed, due to its brittleness, it was generally developed as a copolymer or blend component with other polymers to extend novel nanocomposite (NC) films [15]. PVP has carbonyl groups and are potentially miscible with PVA due to the creation of intermolecular hydrogen bonds. Indeed, the combination of these features allows the formation of polymeric blends that can cause to the preparation of novel biocompatible and homogeneous blend matrices for bio-NC expansion [4,7].

So far, important strides have been made in the field of synthetic PVA-PVP-based nanocomposite. Mallakpour et al. reinforced the PVA/PVP blends using Cu nanoparticles (NPs) through ultrasonic irradiation technique [16]. In other work, Mallakpour et al. prepared PVA/PVP/α-MnO_2-stearic acid NCs and investigated the adsorption behavior of them as adsorbent for Cd (II) ion [17]. Mondal et al. prepared blend NCs PVA/PVP/sodium montmorillonite by sonication [6]. Mudigoudra et al. prepared PVA/PVP/Chitosan ternary polymer blend films by solution blending followed by solvent evaporation technique in the form

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

https://doi.org/10.1016/j.porgcoat.2018.04.023
Received 4 January 2018; Received in revised form 10 April 2018; Accepted 14 April 2018
0300-9440/



Scheme 1. Training scheme of the PVA-PVP/ZrO_2-Th NCs.

of film and investigated the effect of Chitosan on the thermal behavior of PVA/PVP/Chitosan ternary polymer blend films [18]. Abdelrazeka et al. designed PVA/PVP blends filled with lithium bromide using a solvent casting technique [19]. Recently we modified the surface of Zirconia (ZrO_2) NPs and inserted into the PVC [20] and PVA [21] matrix. But, in this study, we prepared the biodegradable blend bio-NC films based on PVA-PVP polymeric blend and modified ZrO_2 NPs with acceptable and prominent properties, by a solution casting method under ultrasound irradiations. Also, the prepared NCs was employed for antibacterial test. The results of analysis indicated that the novel PVA-PVP/ZrO_2-Th NCs has better thermal stability and hydrophilicity than our previous work with single polymers. Change the matrix from one pure to blend will make high differences in terms of physicochem properties and application and would bring new materials for use which each alone could not have it. Another significance and advantage of this study was that all of the materials used were bio-safe and non-toxic with no environmental impact. Also, the energy source used for the preparation of NCs was ultrasonic irradiation which is known as an economical, green, and environmentally friendly tool. On the other hand, PVA and PVP are two of the most widely water soluble polymers and this is an advantage in preparation of NCs based on PVA and PVP which volatile organic solvents removed.

ZrO_2 NP used as nanoreinforcing because of its good thermal resistance, optical absorption, mechanical properties and simple functionalization by various coupling agents [22–24]. To appear characteristic properties of ZrO_2 NP, proper dispersion and good compatibility of them in the PVA and PVP matrices must be achieved. The problem with the using of ZrO_2 is that it easily aggregates in the polymer matrix, so covering the ZrO_2 surface with appropriate molecules can be an effective way in the dispersion process. Thiamine (Th) is a bio-safe and green molecule and because of the unique properties and the presence of $-OH$ and $-NH_2$ groups in its structure were used to modify ZrO_2 NPs to improve dispersal and compatibility of NPs within the PVA and PVP matrices [25]. Then they were characterized and