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A Novel Nano-Fiber of Iranian Gum Tragacanth-Polyvinyl Alcohol/Nanoclay Composite for Wound Healing Applications

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Abstract

The fibers with smaller pores and higher surface area than regular fibers have enormous applications in tissue scaffolds, protective clothing, and wound healing. Iranian Gum Tragacanth (IGT) is the most common natural polymers which has found with lots of applications recently, and has attractive characteristic like nontoxic nature, biodegradability, higher resistance, antibacterial and good biological properties to bacterial attacks. In the current work, poly vinyl alcohol (PVA)/IGT biocomposite fiber is prepared using electrospinning (ELS) method in aqueous solutions with PVA blended system in a volume ratios of 60/40, 70/30, 80/20, and 90/10 composite with different amount of nano-clay (NC) powder (1% and 3%) to enhance the chemical and mechanical stability. The blended nanofibers are characterized by scanning electron microscopy (SEM), fourier transform infrared (FTIR) techniques. The FTIR analysis indicated that PVA and IGT may be having H^+ bonding interactions. The current study reveals that with a higher percentage of IGT in the blend nanofibers, superior degradation, higher chemical and mechanical stability could be obtained. Moreover, the blend nanofibers with 80/20 with 3% NC exhibit improvement in unique properties compared to pure PVA/IGT.

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Keywords: Gum tragacanth; Polyvinyl alcohol; Nano-clay; Electrospinning; Tissue engineering; Wound healing

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1. Introduction

In the last two decades there has been a growing interest in biocompatible and biodegradable natural polymers that are being used to as scaffolds and wound healing for tissue engineering, Venkatesan and Kim (2010). To design soft and hard scaffolds, the main requirements are high porosity, higher wettability, large surface area, and a microenvironment that allows the cells to adhere, proliferate and retain its phenotype. It is well established that pores fibers which are interconnected play an important role in cellular growth; however, with increasing porosity there is an inevitable loss in the biological properties, Rezwan et al. (2006). A large number of different polymers including hydrogels polyvinyl alcohol (PVA), Peppas and Mongia (1997), poly acrylamide (PAC), poly acrylic acid (PAA) have been explored for different biomaterials applications, Langer and Peppas (2003). Among these polymers, PVA have been used for various pharmaceutical applications, Peppas et al. (2006). It also shows a high degree of swelling in water, a rubbery, an elastic nature and therefore closely simulates natural tissue and can be readily accepted into the body, Van Vlierberghe et al. (2011). Another known local polymer, Iranian Gum Tragacanth (IGT) is a dried exudation obtained from the stems and branches of Asiatic species of Astragalus, Mohammadifar et al. (2006). It has been used as an emulsifier, pharmaceutical, and wound healing applications. The IGT is one of the most acid-resistance gums and most efficient natural emulsifier for acidic oil-in-water emulsions. The IGT and PVA represent renewable source and they have no adverse impact on skin and eye irritation, Goswami et al. (2014). Despite the poor mechanical properties of natural polymer nanocomposite, its unique biological properties leads we focus on improving its properties rather than completely replacing it with other biopolymers. Due to their unique characteristics and potential commercial applications of polymer, they have been composite with new generation of bio-ceramics to improve their mechanical properties. The nanoclay (NC) is one of the famous bio-ceramic with good properties, the addition of NC to polymers nanocomposite improves their properties mechanical, biological and chemical characterization, Karamian et al. (2014). The NC biomaterials are reported to have enhanced thermal, mechanical, and biological properties like: diopside, baghdadite and titania, Khandan et al. (2015). Accordingly, in this work we have prepared a new IGT/PVA-NC nanocomposite and evaluated its chemical and mechanical properties due to developing a mechanically strong and highly bioactive material for wound healing applications.

Nomenclature

Mw	Molecular weight
Ɛ	Strain
Ȯ	Tension

2. Materials and methods

2.1. Materials

PVA was purchased from Merck (Co, Germany) with medium (Mw 12000-14000). Also, nano-clay (NC) powder was purchased from Merck (Co, Germany) and milled by mechanical activation process. The NC was ball mills with 500 ml zirconia vial and zirconia balls to homogenize the powder and also the ball to powder weigh ratio (BPR) of 15 and rotational speed of 600 rpm were used for milling process in which the overall mass was 130 g, and milling times were 2 hours. X-ray fluorescence (XRF) of NC presented in (Table 1). It shows that silicon (Si) has the highest element ratio in the composition. Also, there are significant ratios with other elements such as Al, Mg, Ca and Fe. The Iranian GUM tragacanth (IGT) was used from Iranian plant (A. gossypinus). In this study the IGT with high quality ribbon type was collected from plants growing in the mountainous areas (Isfahan province, Iran). Pure powdered IGT with mesh size between 80-400 was used in this study. The purification of IGT has been introduced in the following section.

Table 1. XRF of chemical composition nano-clay powder synthesized by MA process

Composition (wt.%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	Total	Ignition loss
Kaolin	0.17	61.25	20.95	6.40	0.38	0.17	1.61	0.72	0.72	0.12	92.38	13.65

2.2. Purification of IGT

The raw IGT washed with deionized water and dry in sunlight after that ground and sieved. The density value of IGT was 1/42 g/cm^3. Weight 4 g of IGT was dissolved in deionized water and homogenized on the magnetic stirring for overnight then allows standing 12 hours at room temperature. The mucilage was filtrate, separate through a glass funnel. The clear solution was dried through freeze-dried, weight and stored.

2.3. Composite preparation

The polymer solution was prepared by dissolving different ratio 90:10, 80:20, 70:30, 60:40 of PVA/IGT in 100 ml of dionized water. We selected an 80:20 ratio of PVA/IGT, as selective solution and NC had maximum solubility rather than other solvents used for electrospinning. The NC in different concentrations 0.0%, 1%, and 3% (w/w) with respect to PVA/IGT. The effect of NC to the nanobiopolymers was investigated by FTIR analysis. The homogenized NC was then slowly added to the PVA/IGT solution with stirring at room temperature. The solution was allowed to magnetic stirrer for 30 minutes in a sealed container and the mixture was further sonicated for 5 min.

2.4. Electrospinning method

Electrospinning (ELS) technique is one of the major approaches for developing continuous nano-scale fibers with diameters ranging from 10-50 nm. After stirring the solution for 8 hours, NC was added to the composite solutions and agitated for 10 hours. The solutions were stored at 4°C for 6 hours to reach the required homogeneity. The biocomposite solutions were fed into a 20 mL plastic syringe fitted with a needle. The ELS of PVA/IGT with different percentages of NC-enriched was carried out using a the feeding rate of the syringe pump changed from 0.5-1.5 mL/h (flow rate) and high voltage in the range of 10-20 kV was applied using a power supply. The collector plate was made of aluminum (Al) foil, the demission of frame is 10 mm × 50 mm and positioned at a constant distance of 10 cm from the needle. The fabricated soft scaffolds were dried overnight in vacuum to remove the residual solvent (Fig. 1).

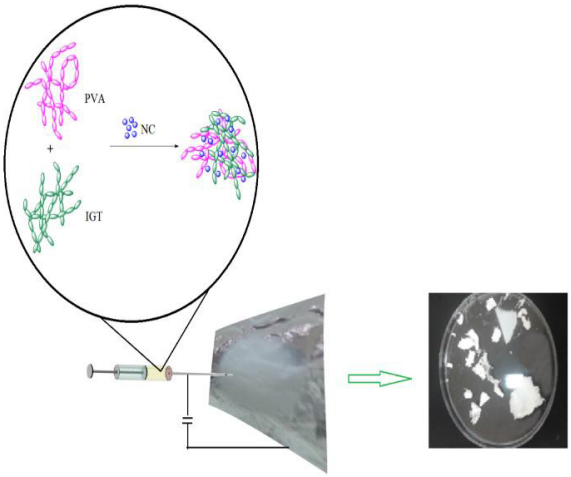

Fig. 1. The ELS method used to produce nanobiocomposite (IGT/PVA-NC).

2.5. Mechanical properties

The mechanical properties of fibers including tensile strength at break is measured by tensile machine (zwick 1446-60, Germany).

2.6. Characterization of the samples

X-ray diffraction (XRD) patterns recorded in the 2θ range of 20-50° with step size of 0.02 Å and a step time of 0.605. In order to investigate the possible change of chemical composition nanofiber were recorded on a FTIR (Perkin–Elmer). The morphology of the fibrous membrane was observed with a scanning electron microscope (SEM) (Philips XL30, Eindhoven, and Netherlands) was used for high-magnification observation. All the samples were coated with gold (Au) using spraying, high vacuum and 40 kV accelerating voltage.

3. Results and discussion

3.1. XRD results

Figure 2 indicates the XRD patterns of the NC powder milled for 2 hours. The peaks broadening can be seen with milling time which is due to crystallite size refinement. It is also notable that the NC powder is completely formed at 2 hours which implies that the homogenize powder has completed at or before this milling time with crystal size less than 30 nm according to modified Scherrer equation, Khandan et al. (2014). Looking at this figure, in addition to widening, NC characteristic peaks (reflections) shows a significant crystalline peak at about 26-28°, which is due to the occurrence of strong sharp.

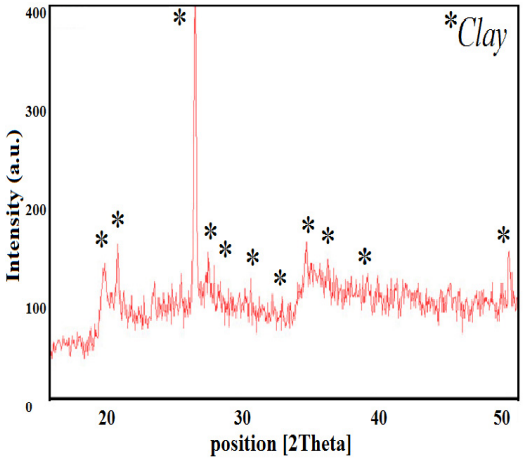

Fig. 2. XRD pattern of NC powder milled for 2 hours in a high-energy planetary ball mill.

3.2. FTIR results

FTIR spectra were also recorded for IGT/PVA and this composite include 0.0%, 1% and 3% of NC (Fig. 3). The characteristic bands at 3442 cm^{-1} was for the stretching frequency of –OH groups as shown in Fig. 3. Asymmetric and symmetric stretching vibrations for methylene groups appeared at around 2930 and 2856 cm^{-1}. A significant band at 1747 is attributed to –C=O group stretching vibrations. The strong peak at 1495 cm^{-1} is ascribed to characteristic asymmetrical stretch of –COO – group. The characteristic asymmetrical stretch of $–COO^-$ group is caused appear bands at 1441 and 1367 cm^{-1}. The spectra showed bands at 11420 cm^{-1} and 1280 cm^{-1}; 1243 cm^{-1} and 1100 $cm^{-1}$for the stretching vibrations of C-O of the polyols, ether and alcohol groups. The strong peak at 1243 cm^{-1} is attributed stretching vibrations of C-O groups. The bands around 2925 cm^{-1} and 2854 cm^{-1} are assigned to asymmetric and the symmetric stretching $–CH_2$ group, respectively.

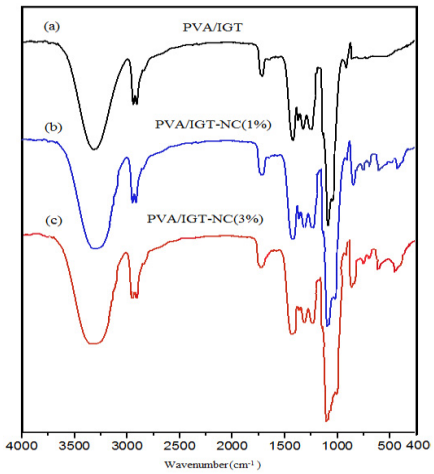

Fig. 3. FTIR spectra of the PVA/IGT with different amount of NC powder (a) 0%; (b) 1%; (c) 3% in the nanobiocomposite.

3.3. SEM analysis

SEM photomicrographs of the PVA/IGT nanocomposite powders at different percentage (0.0%, 1%, and 3%) is shown in Fig. 4. The SEM observation were obtained from fibers which was fabricated from PVA/IGT biopolymer with different amount 10/90, 20/80, 30/70, 40/60, but an optimum nanocomposite sample (20/80) selected to composite with is 0.0%, 1% and 3% NC powder (Fig. 4a,4b,4c). Such fibrous structure would result in a large surface area-to-volume ratio and interconnected porosity. A comparison between the SEM images of the sample with the sample without NC shows in Fig. 4a, it is observed that almost the same surface morphologies are seen with the exclusion that the inter layer spaces are decreased. The composite contains 3% of NC had the highest strength and chemical stability optimized by visual inspection.

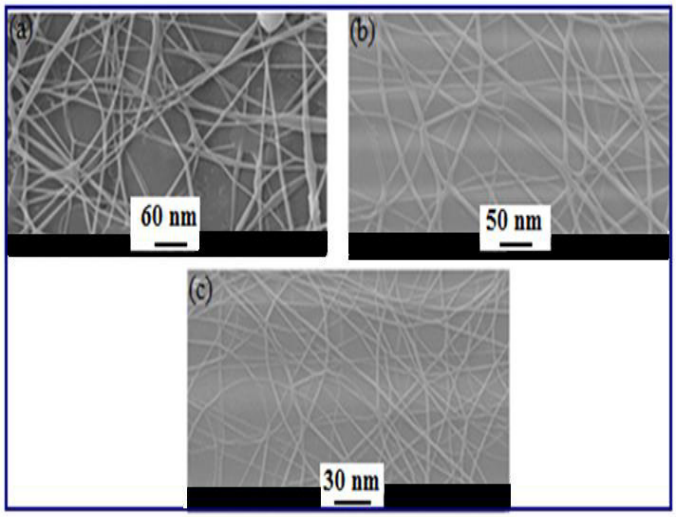

Fig. 4. SEM micrograph of PVA/IGT nanofibers a) 0% (b); 1%; (c) 3% NC powder.

SEM micrographs showed that the blend nanofibers had smaller and narrower diameter distributions with increasing NC content, and their diameter was below 30 nm. Investigations of bioceramics compositing silicate phases like: diopside, Khandan et al, (2015), and akermanite or calcium phosphate phases such as HA and flouorohydroxyapatite (FHA) are enhancing the mechanical properties of the polymers.

3.4. Mechanical properties analysis

The mechanical properties of biocomposite scaffolds were evaluated by tensile testing. The stress-strain curves of the samples are shown in Fig. 5. It is observed that the tensile strength for random PVA/IGT-NC nanofibers is 2.66 MPa and the elastic modulus is 5.22 MPa. By adding more NC to nanofibers, the tensile strength increases to 5.82 MPa with an elastic modulus of 12.2 MPa. Upon mixing with PVA, both the tensile strength and elongation at break are increased with increasing IGT contents.

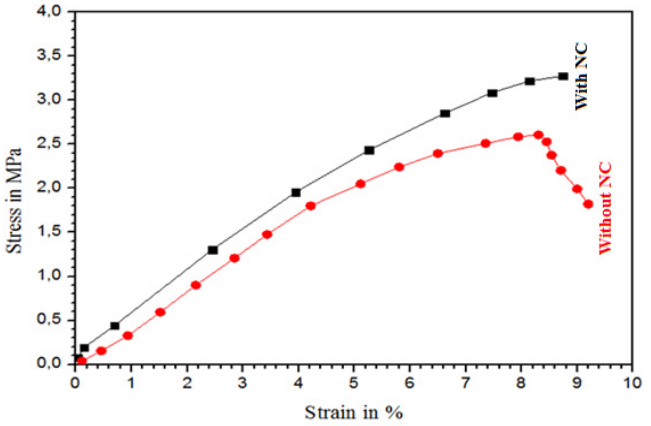

Fig. 5. Diagram of stress and strain of scaffold with and without NC.

4. Conclusions

IGT, PVA was blended with the NC powder to improve the spinnability. The results indicated that, the biocomposite fabricated with smooth surface without any beads. The IGT/PVA ratio varied and nanofibers with the best morphology were obtained at 20/80 IGT/PVA ratios in present certain amount of 3 wt.% NC. The nanofibers average size decreased with adding NC powder to the solution up to 3 wt.%. The FTIR spectra of IGT/PVA blend nanofibers illustrated the characteristic peaks of IGT and PVA. The sample with 3 wt.% of NC powder showed excellent chemical stability and mechanical property against the sample with 0.0% NC powder. Thus, to overcome the poor electrospinnability of IGT solution, synthetic polymers such as PVA solution is blended with IGT solution to improve its spinnability. Furthermore, the blend nanofibers show advancement in mechanical properties compared to pure electrospun PVA with the addition of IGT. Visual inspection properties of IGT/PVA containing 3 wt.% NC revealed that these nanofibers are suitable for wound healing application which can protect the wound surface from infection and dehydration.

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