# Effects of molding temperature, pressure and time on polyvinyl alcohol nanocomposites properties produced by freeze drying technique

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## ARTICLE INFO

## ABSTRACT

The main aim of this study was to develop a novel approach to incorporate high cellulose nanofiber (CNF) loadings into polyvinyl alcohol (PVA) nanocomposites. The nanocomposites were prepared by freezing via liquid nitrogen and consequent freeze drying combined with hot press molding. To investigate the effect of the molding parameters on the morphological, mechanical and thermal properties, chemical structure and transparency of the PVA + CNF nanocomposites, two different mold pressures, temperatures and holding times were used for fabrication of PVA + CNF nanocomposites. The maximum tensile strength of 121 MPa of the PVA + CNF 20% nanocomposites was obtained when they were molded at 130 °C and 50 kPa for 7 min. Dynamic mechanical analysis showed that the storage modulus of the composites prepared at 130 °C and 50 kPa for 7 min is about 20% higher than nanocomposites molded at 150 °C and 150 kPa for 10 min. Optical properties (absorption spectra) of the PVA and PVA + CNF nanocomposites were increased as the mold pressures, temperature and holding time increased. Micrographs showed more sough fracture surface with increasing pressure and temperature during hot press molding.

## 1. Introduction

Cellulose nanofibers (CNF) have received much attention as reinforcement in polymer nanocomposites due to their renewability, biodegradability, low cost, nontoxicity, higher crystallinity, and biodegradable properties (Eslah et al., 2017; Esmaeili et al., 2015; Kiziltas et al., 2015). Currently, the two most widely applied techniques for mixing the CNF with polymers are solution blending and melt compounding methods (Oksman et al., 2016). Casting-evaporation is among the most extensively used technique to produce nanocomposite and many studies of nanocomposite made using this process have been conducted over the last decade (Qua et al., 2009). Considering that the casting-evaporation process is a relatively slow process and is therefore resulting in self-aggregation of the CNF within the matrix, researchers have alternatively used other techniques in order to obtain more rapid evaporation. Another method for the preparation of nanocomposite is melt compounding. In spite of taking advantage of well established processing techniques (Tanahashi, 2010), this method needs exact control of temperature, shear, and residence time when the pre-blend is fed into an extruder in order to prevent fiber degradation (Dondero and Gorga, 2006; Pilla, 2011). Another difficulty in melt compounding of nanocomposites is achieving uniform dispersed nanoreinforcements in the polymer matrices (Mittal, 2011). Therefore, there is a need to develop low-cost and simple method to fabricate CNF nanocomposites with uniformly dispersed CNF. The alternative method is consisting of freeze-drying and hot-pressing or freeze-drying, extruding and hot-pressing the mixture (Dufresne, 2010). Process parameters (temperature, pressure and heating time) used in a hot-pressing process play an important role in the properties and interfacial characteristics of the nanocomposites (Govindaraju et al., 2014; Senthil Kumar and Balachandar, 2014). Since, the high temperature and pressure may lead to natural fiber and polymer degradation, consequent decrease in volume fraction of the reinforcement phase in the final composite and thus deterioration of the properties (Deng et al., 2010). Therefore, the processing parameters must be carefully selected in order to yield the optimal composite properties. Even if the polyvinyl alcohol (PVA) nanocomposites have been a popular research topic, we think that there is acknowledge gap on how the processing is affecting the composites structure and properties. Therefore, the aim of the present study was to establish a new rapid technique for the fabrication of highly homogeneous PVA + CNF nanocomposites with different content of CNF using liquid nitrogen and freeze drying technique. In addition, the

effects of the molding parameters on mechanical and thermal properties and appearance of the resulted nanocomposites (loaded with 5, 10, 20 and 30 wt% CNF) were characterized.

## 2. Experimental

### 2.1. Materials

PVA with a molecular weight of $M_w$ = 145, 000 g/mol and hydrolysis degree of 89% was supplied by Merck KGaA (Darmstadt, Germany). Cellulose nanofibers, as a white gel with diameter of 23 ± 10 nm and produced by passing the water slurry of 1 wt% canola straw fibers through a MKCA6–3 grinder (Masuko Sangyo, Kawaguchi, Japan) at 1500 rpm, were purchased from Nano Novin Polymer Company (Sari, Iran).

### 2.2. Manufacturing methods

In the present study, PVA + CNF nanocomposites were prepared by using flash freezing of PVA + CNF suspension in liquid nitrogen followed by freeze drying technique and hot press molding. To investigate the influence of the molding parameters on the properties of the PVA + CNF nanocomposite films two various processing conditions were considered. One set of the PVA + CNF nanocomposites was molded at a high temperature and pressure for a long time with cold press (process 1), while another one at a low temperature and pressure for a short time with cold press (process 2). PVA (10 g) was dissolved in distilled water (120 ml) at 50 °C with continuous stirring by magnetic stirrer at 1200 rpm for 3 h. After the dissolution, desired volume of nanofiber suspension was added to the solution (shown in Table 1). The solution was poured onto plastic petri dishes, flash-frozen in liquid nitrogen for 2 min. The samples were then freeze dried (Lyotrap, UK) at

− 45 °C for 24 h, until most of the water was eliminated by the sublimation. Then, the PVA + CNF nanocomposites were compression molded using two processes.

In the present study, response surface methodology was used to optimize the compression molding parameters of CNF reinforced PVA composites by selecting three variables (temperature, time, and pressure) as independent variables and tensile strengths and thermal properties, as dependent ones. The process was optimized through magnified contour analysis. It is noticeable to say that the results of the modeling and the optimization of the process (response surface methodology and the magnified contour analysis), will be presented in another future work. According to the analysis, two sets of process parameters were obtained as optimum conditions and compared to each other. In the first process, the test samples were pre-pressed at 150 °C for 2 min to remove air and then hot pressed under 150 kPa at 150 °C for 10 min. At the end of the process, the films were cooled at 100 kPa and 20 °C for 1 min. In the second process, the test samples were fixed between an aluminum foil and fireproof paper and placed in the hot press at 130 °C for 5 min without any pressure, and then compression molded under 50 kPa at 130 °C for 7 min. Finally, the pressed films were cooled to 20 °C for 2 min without any pressure. In general, thermal degradation of PVA usually starts at about 150 °C. Applying higher temperature leads to a nonreversible reduction of PVA strength and consequently, a decrease in the mechanical properties of the fabricated nanocomposite. At very low temperature of processing, a long time of press is needed for the air bubbles to be removed from the molded films. So, obtaining these values as the optimum points is not unexpected.

The press conditions used to prepare the PVA and PVA + CNF nanocomposites are summarized in Table 2 and Fig. 1 represents a schematic about the preparation process of the nanocomposite.

## 3. Characterization

### 3.1. Scanning electron microscopy

Microstructural characterization of the neat PVA and the PVA + CNF nanocomposites was investigated using Zeiss Ultra 55 Scanning Electron Microscope (SEM) (Carl Zeiss, Oberkochen, Germany). The fracture surfaces of the tensile test samples were sputter coated with a thin layer of gold, at a voltage of 1 kV and a discharge current of 10 mA for 120 s before SEM. Images were taken at an acceleration voltage of 5 kV.

**Table 1**
Material formulations in the final compositions.

| Materials | PVA (g) | CNF (g) | Composition (%) |
|---|---|---|---|
| PVA | 10 | 0 | PVA (100) |
| PVA + CNF5 | 9.5 | 0.5 | PVA + CNF(95/5) |
| PVA + CNF10 | 9 | 1 | PVA + CNF (90/10) |
| PVA + CNF20 | 8 | 2 | PVA + CNF (80/20) |
| PVA + CNF30 | 7 | 3 | PVA + CNF (70/30) |

**Table 2**
Press conditions used to prepare the PVA and PVA + CNF nanocomposites.

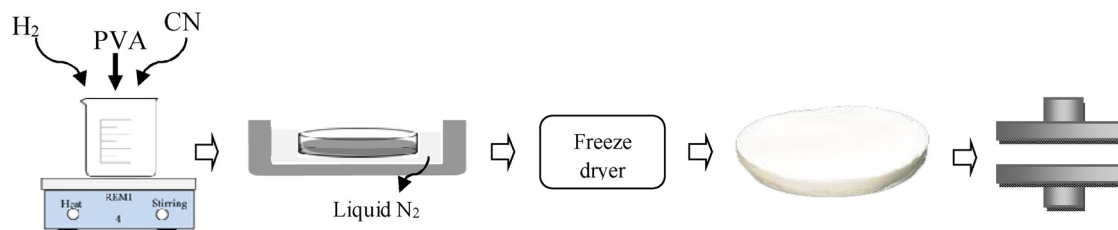| Press conditions | Pre-pressed | | Press | | | Cold press | | |
|---|---|---|---|---|---|---|---|---|
| | Temp (°C) | Time (Min) | Pressure (KPa) | Temp (°C) | Time (Min) | Pressure (kPa) | Temp (°C) | Time (Min) |
| Process1 | 150 | 2 | 150 | 150 | 10 | 20 | 100 | 1 |
| Process2 | 130 | 5 | 50 | 130 | 7 | 0 | 20 | 2 |



**Fig. 1.** Schematic representation of construction of the nanocomposite, including mixing of the materials, freezing using liquid nitrogen, freeze drying and compression molding.