Preparation and characterization of thermoplastic starch and cellulose nanofibers as green nanocomposites: Extrusion processing

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ABSTRACT

This research was aimed at studying the preparation of thermoplastic starch (TPS) from cornstarch flour using twin screw extrusion. Also, the effects of the addition of cellulose nanofibers (CNFs) as reinforcement, on TPS nanocomposite films properties were evaluated. Nanocomposites with 0.5, 1.0 and 1.5 wt% of CNFs content were prepared. The chemical structure of starch, TPS and TPS/CNFs were characterized by Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction. The mechanical properties, morphological structure, and thermal stability of neat thermoplastic starch and their nanocomposites were investigated by scanning electron microscopy (SEM), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and water absorption (WA) test. Results showed that it was possible to improve the WA, thermal, and mechanical properties of TPS with the addition of CNFs due to its good dispersion and the interaction of CNFs with the TPS matrix. The storage modulus, loss modulus, and the tan δ peak position of TPS/CNF nanocomposites improved in comparison with the TPS matrix. These findings confirmed the enhancement of mechanical properties of TPS/CNF nanocomposites. In addition, TGA and DSC results showed that increasing CNF content improves the thermal stability of TPS-based nanocomposites. SEM images showed that CNFs dispersion within the TPS matrix was uniform and the surfaces of TPS/CNF films were smooth. The WA of the TPS/CNF composites moderately decreased with the addition of CNFs. Finally, the results obtained clearly showed the advantages of reinforcing TPS with CNFs, a natural, cheap and abundant green nanocomposite.

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1. Introduction

Concerns over the depletion of fossil fuels, climate change, variability reduction in feedstock costs relative to petroleum-based building blocks, and pressure from various constituents on increasing the renewable carbon content in plastics has driven interest in developing bio-based polymers. Thermoplastic starch (TPS) is a biodegradable polymer that has been increasingly attractive in both academic and industrial sectors in recent years [1,2]. Native starch is converted into TPS under heat and shear in the presence of plasticizers (such as water, glycerol, sorbitol, etc.) [3]. Under these conditions, the starch granules are destructurized, plasticized, and melted forming a material that has similar behavior to that of thermoplastics [4]. The crystallinity of starch granules disappears during the above-mentioned process and an amorphous material is ultimately obtained [5]. Compared to common thermoplastic polymers, TPS has three main disadvantages including poor mechanical properties, low thermal stability, and high water

sensibility [6]. Several solutions have been investigated to minimize or even overcome these drawbacks. These solutions involve (i) the chemical modification of starch (esterification and cross-linking), (ii) mixing with other polymers such as poly(vinyl alcohol) and biodegradable polyesters such as poly(e-caprolactone), polyesteramide, and poly (butylene succinate adipate), and (iii) use of different types of fibers or microfibrils in association with TPS [6].

Nowadays, cellulose nanofiber (CNF) is one of the most promising reinforcing materials for improving mechanical properties and moisture absorption of TPS because of its abundance, high aspect ratio, low weight, high strength and biodegradability [2]. CNFs are typically separated from lignocellulosic plants, such as wood and agricultural crops, using mechanical and chemical treatments. Unlike the cellulose nanowhiskers prepared by acid hydrolysis, CNFs contain both the amorphous and crystalline regions of cellulose and can therefore create entangled networks [7]. Furthermore it is also a polysaccharide containing repeating unit of glucose similar to starch [4].

The most conventional method used in the preparation of TPS/CNF nanocomposites has been solution casting of a dilute slurry of TPS matrix and nanofibers. For large scale production, this method is

slow and expensive [7]. Extrusion compounding is the most interesting methods for industrial processing due to easy scale-up and the possibility of further molding of the materials. Thus, the main goal of this work was to study the extrusion processing of TPS reinforced with CNFs. In fact, the novelty of this work is using the extrusion method for preparation of TPS and TPS/CNF nanocomposites, which has not been previously reported. The TPS were characterized by Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). Then, the effects of CNFs addition and its concentration on the properties of TPS/CNF nanocomposites were studied. The morphology and properties of the resulting nanocomposites were characterized by scanning electron microscopy (SEM), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and water absorption (WA).

2. Materials and methods

The preparation of the TPS (matrix) and TPS/CNF nanocomposites, as well as the materials used are described below. The TPS and TPS/CNF samples were characterized by XRD, SEM, TGA, DMTA, WA and DSC. It should be noted that each value obtained represents the average of at least 3 samples.

2.1. Materials

TPS was prepared from industrial unmodified starch obtained from corn, with a 25% content of amylase and 75% amylopectin (Glucosan Co., Iran). The CNF gel (with 2.7% solid mass) used in this study was a product of the Nano Novin Polymer Co. (Iran), and used as reinforcement at various proportions ranging from 0.5% to 1.5 wt% referred to the TPS. Reagent grade glycerin as plasticizer was used to prepare the TPS. It was obtained from the local market.

2.2. Preparation of TPS and TPS/CNFs nanocomposites

The neat TPS and the subsequent TPS/CNF nanocomposites were prepared using a two-step process. In the first step, the main components of the matrix (corn starch and glycerol) were manually premixed in polyethylene bags for 5 min. Subsequently, the resulting blend was further mixed with the corresponding amount of CNFs for 10 min. All the blends were made with a starch to glycerol mass ratio of 70/30 (w/w). Three formulations of TPS/CNF nanocomposite films, i.e. TPS/CNF$_{0.5}$, TPS/CNF$_{1.0}$ and TPS/CNF$_{1.5}$, containing different CNF contents of 0.5, 1.0 and 1.5 wt%, respectively, were prepared. The extrusion was carried out using a co-rotating twin-screw extruder (ZSK-25, Germany), with a screw speed of 80 rpm. The barrel temperatures of the extruder were controlled at 80, 100, 110, 115 and 120 °C for zones 1, 2, 3, 4 and 5, respectively, while the temperature of the die was set at 125 °C. Feeding of the prepared premixes was done manually due to the small amounts of materials. The extruded strand was passed through a water bath, granulated, and dried at 105 °C for 24 h. In the second step, the resulting granules were subsequently compression-molded to produce the samples according to ASTM standard. The dimensions of the mold were $100 \times 100 \times 1$ mm^3. Typical molding conditions were: press temperature 190 °C, pressure during heating 3.5 MPa, heating time 10 min and cooling time 5 min.

2.3. Characterization

2.3.1. XRD

The crystallinity of neat TPS and TPS/CNF nanocomposites was recorded on an X-ray diffractometer, X'pert Pro MPD, PAnalytical, 2009, (Netherland), with CuKa radiation (wavelength of 1.5405 Å). The measurements were carried out in 2θ ranges between 5 and 80° with step

size of 0.026° and time per step 99.45 s. The crystalline index of cellulose, C_{Ir}, was calculated using Eq. (1).

$$C_{Ir} = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \tag{1}$$

where I_{200} is the peak intensity corresponding to cellulose I, and I_{am} is the peak intensity of the amorphous fraction.

2.3.2. Scanning electron microscopy (SEM)

The dispersion and distribution of CNFs into the TPS matrix were analyzed by a field emission scanning electron microscopy (FE-SEM) with a TESCAN (model MIRA 3 LMU) equipment. The acceleration voltage was 10 kV and the specimens were sputter-coated with gold to avoid charging.

2.3.3. Thermogravimetric analysis

The thermal stability of TPS and TPS/CNF nanocomposites was monitored by thermogravimetry analysis (TGA) and differential thermogravimetry (DTG). The equipment used was a Pyris 1, Perkin-Elmer (Germany). The measurements were carried out at a heating rate of 10 °C/min from ambient temperature to 600 °C. All runs were carried out under nitrogen atmosphere in order to prevent any thermo-oxidative reaction. The sample's weight was approximately 15 mg.

2.3.4. Differential scanning calorimetry (DSC)

DSC was used to measure the thermal transitions of TPS and TPS/CNF nanocomposite films. The test was performed with a Pyris 1, Perkin-Elmer (Germany) differential scanning calorimeter equipment, fitted with a nitrogen based cooling system. All the measurements were performed in the temperature range of −50 to +250 °C at a heating rate of 10 °C/min.

2.3.5. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis was carried out using a DMA 800, TA analyzer (Perkin-Elmer), in 3-point bending mode. The testing temperature was varied from −100 to +150 °C at a constant test frequency of 1 Hz and heating rate of 5 °C/min. The values of storage modulus (E'), loss modulus (E''), and loss factor (tan δ) were recorded.

2.3.6. Water absorption test

Water absorption test was performed in accordance with the ASTM standard E104. All the specimens for water absorption were cut from TPS and TPS/CNF nanocomposite films with dimensions of 2×2 cm^2 and dried at 60 °C for 24 h. The dried samples were placed in a desiccator containing calcium sulfate (RH = 0%) for 3 days and afterwards the initial weight of the samples were measured. The samples were then transferred into a desiccator containing potassium sulfate (RH = 98%) and the time taken to reach a constant weight was marked. The water absorption (WA) of the specimens was calculated as follows:

$$WA = \frac{W_1 - W_0}{W_0} \times 100 \tag{2}$$

where W_1 is the weight of the sample at the time in 98% RH and W_0 is the initial sample weight exposure to 98% RH.

3. Results and discussion

3.1. Crystallinity

Fig. 1 shows the diffractogram corresponding to the cornstarch, TPS and TPS/CNF$_{1.5}$. The results displayed in Fig. 1 demonstrate important changes in the structure of the starch after processing. The analysis of the native starch showed a predominance of type A crystallinity,