Carbohydrate Polymers 197 (2018) 305–311

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Thermoplastic starch foamed composites reinforced with cellulose nanofibers: Thermal and mechanical properties

Abbas Ghanbari[a], Taghi Tabarsa[a], Alireza Ashori[b,*], Alireza Shakeri[c], Mahdi Mashkour[a]

[a] Department of Wood Engineering and Technology, Gorgan University of Agricultural Sciences & Natural Resources, Gorgan, Iran
[b] Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), P.O. Box 33535111, Tehran, Iran
[c] School of Chemistry, University College of Science, University of Tehran, Tehran, Iran

ARTICLE INFO

Keywords:
Thermoplastic starch
Foam
Cellulose nanofibers
Thermo-mechanical properties

ABSTRACT

The present work reports the effect of cellulose nanofibers (CNFs) on the thermal, dynamic mechanical analysis (DMA), density and water uptake of thermoplastic starch (TPS) foamed composites. The obtained thermal and DMA results illustrate that thermal stability, storage modulus (E'), loss modulus (E'') and damping factor (tan δ) increase for all TPS/CNF samples compared to the pure TPS foamed composite. The results showed that the incorporation of CNFs caused an increase in the glass transition temperature (T_g) of the TPS foamed composites. Additionally, thermal results revealed that 1.5 wt% CNF offers superior resistance or stability towards heat compared to its counterparts. Addition of the CNF filler into the TPS matrix decreased the apparent density and water absorption. Interestingly, SEM images illustrate that when a small content of rigid nano particles (1.0 or 1.5 wt%) was added in the foamed composites, the cell size decreased while the cell density increased.

1. Introduction

Over the past few years, replacement of petroleum derived polymers with bio-based ones has been one of the most important trends in the polymer field (Mihai, Huneault, Favis, & Li, 2007). Among the natural polymers, thermoplastic starch (TPS) is very attractive material due to its availability, relatively low cost and its appealing physical and mechanical properties (Balakrishnan, Sreekala, Kunaver, Huskić, & Sabu, 2017). For this reason, nearly 85–90% of the bioplastics found on the market are made from starch. However, compared to the common thermoplastic polymers, TPS has some drawbacks including low thermal stability and high water sensibility (Glenn, Imam, & Orts, 2011). In addition, TPS films are brittle due to the strong intermolecular and intramolecular hydrogen bonding between the starch chains. A commonly used approach to overcome these drawbacks is to melt blend TPS with additives or reinforcing agents (such as emulsifiers, kaolin, pectin, cellulose nanofibers (CNFs), bark, and others) to form composite materials (Balakrishnan, Gopi, Sreekala, & Thomas, 2018; Mitrus & Moscicki, 2014).

It should be noted that the properties of composites depend greatly on the composition and nature of the blended components, enabling fine-tuning of properties that could potentially suit a wide range of applications. Bénézet, Stanojlovic-Davidovic, Bergeret, Ferry, and Crespy (2012) studied the physical and mechanical properties of starch foam reinforced by natural fibers. Results reported in this work showed that addition of 10 wt% hemp fibers exhibited the best properties, including maximal resistance and a notably reduced water absorption.

Foamed polymer composite, a group of lightweight materials full of pores in the microstructure, has been used for many applications where its unique properties such as lightweight, excellent thermal and/or acoustical insulation, and cushion protection are of value (Hu, Lin, Chang, & Huang, 2015). This technology has expanded the market for composite foams by broadening their applications because of the breakthrough in the production of value-added products with complex geometrical structure (Raps, Hossieny, Park, & Altstädt, 2015). The high expansion ratio induced by foaming process generally reduces the material cost and consumption in large-scale produced plastic parts without a major compromise to the required properties. TPS-based foam can be produced by many techniques, including extrusion or hot mold baking (Kaisangsri, Kerdchoechuen, & Laohakunjit, 2012). However, application of extrusion technique to process TPS mixtures can be one of the most economical and efficient way to produce TPS foam composites (Mitrus & Moscicki, 2014).

Although many reports have been published about TPS-based foams, there are few studies on TPS-based foam reinforced with CNFs. Hence, the aim of this work was to carry out a comparative study of the

* Corresponding author.
E-mail addresses: ghanbari@gau.ac.ir (A. Ghanbari), tabarsa@gau.ac.ir (T. Tabarsa), ashori@irost.ir (A. Ashori), alireza.shakeri@ut.ac.ir (A. Shakeri), mashkour@gau.ac.ir (M. Mashkour).

https://doi.org/10.1016/j.carbpol.2018.06.017
Received 6 February 2018; Received in revised form 18 May 2018; Accepted 4 June 2018
Available online 06 June 2018
0144-8617/

influence of the CNFs addition on TPS nanocomposites foams using extrusion process. The morphology and properties of specimens were characterized by scanning electron microscopy (SEM), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and moisture absorption (MA).

2. Materials and methods

2.1. Materials

Native corn starch (Glucosan Co., Iran) was dried to about 5% moisture content prior to extrusion. The CNF gel (with 2.7% solid mass) used in this study was a product of the Nano Novin Polymer Co. (Iran). Reagent grade glycerin as plasticizer was used to prepare the TPS. It was obtained from Duksan Co. (South Korea). Azodicarbonamide (AZD) was purchased from Kum Yang (South Korea) as an exothermic chemical blowing agent. It has a specific gravity of 1.261 g/cm^3, decomposition temperature of 200–205 °C, and purity of 99%. Zinc oxide (Tetra Kum Co., South Korea) was used as a catalyst (kicker) to decrease the decomposition temperature of the blowing agent to 170 °C.

2.2. Preparation of foamed composites

Formulations of the premixes and abbreviations used for the respective premixes prepared are given in Table 1. The neat TPS and the subsequent foamed composites were prepared using a two-step process. In the first step, the main components of the matrix (starch and glycerin) were manually premixed in polyethylene bags for 5 min. Subsequently, the resulting blend was further mixed with the corresponding amount of CNFs, AZ and ZnO, for 10 min. A co-rotating twin-screw extruder (ZSK-25, Germany) was used for extrusion. Screw speed was fixed at 80 rpm for all formulations. The temperature profile during extrusion was 80/100/110/115/120/125 °C from the barrel section just after the feed throat to the die. After attaining the steady state, prepared premixes were fed manually into the extruder feed throat. The extrudates were 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 D4703 standard. The dimensions of the mold were 100 × 100 × 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. Characterizations

2.3.1. Scanning electron microscopy (SEM)

Foam morphology (cell volume and cell density) was characterized using 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. The cell density (N_f), defined as the number of cells per unit volume (cm^3) of the foamed composites can be calculated using Eq. (1):

$$N_f = \left(\frac{NM^2}{a}\right)^{3/2}\left[\frac{1}{1-V_f}\right] \quad (1)$$

Table 1
Compositions of obtained TPS and TPS/CNF foamed composites.

ZnO (wt %)	AZD (wt %)	CNF (wt %)	Glycerin (wt%)	Starch (wt %)	Code
1.0	2.0	0.0	30	67.0	TPS
1.0	2.0	0.5	30	66.5	TPS/CNF$_{0.5}$
1.0	2.0	1.0	30	66.0	TPS/CNF$_{1.0}$
1.0	2.0	1.5	30	65.5	TPS/CNF$_{1.5}$

where N is the number of cells in the SEM images, M and a are the magnification factor of the micrograph and the area of the micrograph (cm^2), respectively (Matuana, Faruk, & Diaz, 2009). Cell volume (V_f) of the foamed composites can be expressed by Eq. (2):

$$V_f = 1 - \frac{\rho_f}{\rho} \quad (2)$$

where ρ_f and ρ are the densities of foamed composites and TPS material.

2.3.2. Thermogravimetric analysis

The thermal stability of TPS and TPS/CNF foamed composites 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.

2.3.3. Differential scanning calorimetry (DSC)

DSC was used to measure the thermal transitions of TPS and TPS/CNF foams. 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.

2.3.4. 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 damping factor (tan δ) were recorded.

2.3.5. Apparently density

The apparent density was determined according to ASTM D 1622, which analyzes the ratio between the mass and volume of foamed samples in triplicate. The measurements of length, width and thickness were made in triplicate for each foamed sample.

2.3.6. Water uptake

The water uptakes of foamed specimens were measured according to ASTM D E104. All samples with dimensions of 2 × 2 cm^2 were dried at 60 °C for 24 h. The dried samples were placed in a desiccator containing calcium sulfate (RH = 0%) for three 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 analysis was made in triplicate for each treatment.

3. Results and discussion

3.1. Microstructure and cell morphology

The microstructure and cell properties will determine the performance of foamed composites. The scanning electron microscopy (SEM) was used to analyze the cross sections of obtained TPS-based foamed composites in order to determine the cell density, void size and shape. According to the literature references the introduction of solid particles such as CNFs into the TPS premix can significantly change the foam growth process by affecting the initial nucleation step (Babaee, Jonoobi, Hamzeh, & Ashori, 2015; Dufresne & Castano, 2017; Saba et al., 2017). Fig. 1 illustrates the cross-sectional morphologies of the foamed composites containing different concentrations of the CNFs (0, 0.5, 1.0, 1.5 wt%). As it can be seen, the cell properties will be significantly affected by the rigid nano fillers. In comparison with TPS