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Mechanical properties and thermal characteristics of poly(lactic acid) and paraffin wax blends prepared by conventional melt compounding and sub-critical gas-assisted processing (SGAP)

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ABSTRACT

In this study, poly(lactic acid) (PLA)/paraffin wax (PW) blends containing different amounts of PW were investigated. The blends were prepared by a twin-screw extruder using two different methods: conventional melt compounding extrusion and sub-critical gas-assisted processing (SGAP). Then, the blends and neat PLA were injection molded into ASTM 638 Type V tensile bars for evaluation. To observe the effects of the different melt compounding processes and the effects of paraffin wax added to the blends, the rheological properties, crystallization behavior, and thermal stability of the extruded blends, as well as the phase morphology and tensile properties of the injection molded tensile bars, were characterized. The results showed that the addition of paraffin wax yielded tremendous improvements in elongation compared to neat PLA. In addition, samples made by the sub-critical gas-assisted processing (SGAP) extrusion method exhibited more homogeneous phase morphologies and paraffin wax dispersion, better tensile properties and thermal stability, and more consistent material properties as compared to their conventionally compounded counterparts.

1. Introduction

In anticipation of the eventual depletion of petroleum resources, and in consideration of the environment as well as special biomedical applications, the plastics industry is increasingly interested in biomaterials. Poly (lactic acid) (PLA) is one of the most widely used bioplastics for various end-use applications, including food packaging, medical devices, transportation, structural applications, and disposable utensils [1–3]. PLA is a biocompatible and biodegradable polyester that can be made from renewable resources such as starch, cellulose, roots, or sugar [4]. Unfortunately, PLA is inherently brittle and exhibits low impact strength, slow crystallization rates, and has low thermal resistance. In addition, PLA melt is also very viscous. All of these shortcomings limit the potential applications of PLA. To overcome these challenges, PLA has been modified in several ways to increase its processability, mechanical properties, and crystallization kinetics [5–7]. Such modifications include blending it with other fillers and polymers such as organic montmorillonite (nanoclay) [8], graphene [9], bamboo fibers [10], carbon nanotubes [11], polypropylene (PP) [12], polystyrene (PS) [13], poly-tetrafluoroethylene (PTFE) [14], and poly(ε-caprolactone) (PCL) [15].

Waxes like jojoba oil have been used as a plasticizer in PLA [16]. In this study, paraffin wax (PW) was chosen as a filler to improve the processability and ductility of PLA. Paraffin wax has been widely used in lost-wax casting [17,18] and investment casting [19,20] to improve the precision and surface finish of the metallic components. This is because paraffin wax is chemically inert, has stable mechanical properties, is an excellent lubricant, is commercially available at a low cost [21], and undergoes ductile failure at low strain rates [8]. However, to the best knowledge of the authors, paraffin wax has never been used with PLA to modify its processability, mechanical properties, and crystallization kinetics. This is also the first attempt to employ a special “sub-critical gas-assisted processing (SGAP)” process to improve the mixing of PLA with paraffin wax.

In order to disperse paraffin wax in PLA, a twin-screw extruder was employed to melt-compound PLA and paraffin wax at different weight ratios. In addition, the special SGAP extrusion was employed in an attempt to achieve better dispersion of paraffin wax in PLA. This SGAP method introduces nitrogen (N_2) or carbon dioxide (CO_2) in a sub-critical state into the extruder barrel to facilitate dispersion of the paraffin

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wax by adding elongational stresses through bubble expansion during extrusion of polymer pellets [22,23]. Basically, foaming involves bubble nucleation and bubble growth (phase separation), resulting in visible gas bubbles dispersed in a continuous matrix [24]. The main advantage of the SGAP process is to use a simple set-up to disperse the filler by introducing foaming during the extrusion process, which typically occurred when the injection gas pressure is about 0.35 MPa (50 psi) above the melt pressure at the die exit. Therefore, it is not designed to measure the exact amount of nitrogen introduced to the melt. In the SGAP process of this study, the gas was set to 0.35 MPa (50 psi) greater than the measured melt pressure at the die exit, which was 1.03 MPa (150 psi), thus making the gas pressure 1.38 MPa (200 psi). This was well below the supercritical pressure for N_2 3.39 MPa (492.4 psi) [25]. SGAP is a low cost process that only requires simple equipment—such as a standard gas cylinder, regulator, metering pump, and metal hoses—compared to more expensive supercritical fluid (SCF) injection or extrusion equipment. The resultant foamed pellets can be subsequently processed to produce either solid or foamed components, depending on the processing method and how much gas (as a blowing agent) remaining inside the pellets.

In this study, PLA was melt compounded with paraffin wax at ratios of 20%, 35%, and 50% by weight to modify PLA's mechanical properties. After pelletizing, two different kinds of pellets were obtained, depending on the melt compounding method; i.e., conventionally melt compounded solid pellets and SGAP-foamed pellets. Pellets prepared by SGAP are labelled with a prefix "F-". Solid tensile bars were then injection molded with these two different pellets. Although foamed pellets from the SGAP process were used for injection molding, the premolding drying and elapsed time from melt compounding to injection molding (about three weeks) allowed the gas to diffuse out from the SGAP-foamed pellets prior to injection molding. In addition, the plastication within the injection molding barrel and the pack/hold pressure eliminated any trapped air or pre-existing voids, thereby producing solid tensile test bars. Thermal investigations were performed to study the effects of paraffin wax as a filler of PLA. Stress–strain behavior and SEM were also used to characterize the tensile properties and morphology of the PLA/PW blends, respectively. The effect of paraffin wax on the rheological behavior of the extruded PLA/PW blends was also studied.

2. Experimental methods

2.1. Processing

2.1.1. Materials

Ingeo 3001D—an injection grade PLA in pellet form—was purchased from NatureWorks (Minnetonka, MN). It has a MFR of 22 g/10 min (ASTM D1238), a density of 1.26 g/cm^3, and a 1.4% D-LA content. Purified paraffin wax beads were obtained from LorAnn Products (Michigan, MI) with a density of 0.88 g/cm3. They arrived as white, odorless beads and were used as received. Due to paraffin wax belongs to the ethylene group and it has similar properties to polyethylene. Nitrogen (purchased from Airgas) was used as the physical blowing agent for the sub-critical gas-assisted processing (SGAP) extrusion process.

2.1.2. Equipment

Mixing of the blends was performed using a Leistritz ZSE-18 corotating twin screw extruder with a screw diameter of 18 mm and an L/D ratio of 42. For the SGAP process, a standard nitrogen cylinder and a pressure regulator purchased from Airgas were connected to the barrel of the extruder by a metal hose (1/8″ diameter) with Swagelok fittings. To ensure the same thermal–mechanical history, neat PLA was also processed using the same conventional melt compounding and SGAP processes. Before extrusion, PLA pellets were dried in a vacuum oven at 80 °C for 6 h to remove any moisture. Prior to the injection molding process, the extruded pellets were again dried in a vacuum oven at 40 °C for 24 h. ASTM 638 Type V tensile bars were injection molded using an Arburg Allrounder 270A injection molding machine. Some key processing conditions are listed in Table 1. The metering pump capacity was selected to provide multiple injections of small volumes of nitrogen in an effort to achieve continuous flow. Otherwise, bubble collapse and coalescence in the extrudate would occur, which is undesirable. In this study, the pump starts only after the screw is filled and pressure at the screw tip has reached the normal operating level in order to avoid forward or backward flow of the physical blowing agent [24].

Table 1
Key process conditions.

Extrusion			
Temperature (°C)	155/155/160/165/170/175/180 (sequence from hopper to die)		
Screw speed (rpm)	100		
Feed rate (g/min)	30		
SGAP injection pressure (psi)	200		
Injection molding			
Nozzle temperature (°C)	180	Mold temperature (°C)	25
Injection speed (cm^3/s)	45	Injection pressure (bar)	900
Back pressure (bar)	50	Cooling time (sec)	45
Pack/hold pressure (bar)	500	Pack/hold time (sec)	7

2.2. Characterization

2.2.1. Gel permeation chromatography (GPC)

Molecular weights and polydispersity indices of unprocessed PLA and compounded PLA were determined by VE 2001 gel permeation chromatography (GPC) equipped with a 302 tetra detector array in order to investigate the potential degradation of the materials from each of the procedures. Tetrahydrofunan (THF, HPLC grade, Fisher Scientific) was used as an eluent and the flow rate was set at 1 mL/min with an injection volume of 100 µL. All test solutions were prepared at a concentration of 2.5 mg/mL.

2.2.2. Differential scanning calorimetry (DSC)

Thermal characterization of extruded neat PLA and blends was performed using a TA Instruments Q20 with sealed aluminum pans and a constant nitrogen flow of 50 ml/min. All samples were taken from the extruded (conventional and SGAP) pellets and were within 5–10 mg. The DSC profile was of a heat/cool/heat cycle from 25 °C to 200 °C at a rate of 5 °C/min under a nitrogen protective atmosphere. The first heating curve stayed at 200 °C for 5 min to erase any previous thermal history.

The degree of crystallinities (X_c) of the neat PLA was evaluated from their corresponding melting enthalpies using Eq. (1) [26]. The 100% crystalline melting enthalpies for PLA was taken as 93.0 J/g [27],

$$X_c = \frac{\Delta H_m - \Delta H_{cold}}{\Delta H_{m100} * W_f} \times 100\% \tag{1}$$

where ΔH_m is the measured melting enthalpy of the blend, ΔH_{cold} is the cold crystallization enthalpy, ΔH_{m100} is the melting enthalpy of the 100% crystalline PLA, and W_f is the weight fraction of PLA in the blends.

2.2.3. Thermogravimetric analysis (TGA)

TGA analyses of all extruded neat PLA and PLA/PW blends were performed using a TA Instruments Q50 with a platinum pan at a constant nitrogen flow rate of 50 ml/min with a temperature ramping from 25 °C to 600 °C at a rate of 10 °C/min to measure weight loss. The residual weight of the specimen as a function of the temperature was also recorded.