PREPARING, CHARACTERIZING, ON-LINE DIGITAL IMAGE PROCESSING OF RESIDENCE TIME DISTRIBUTION AND MODELING OF MECHANICAL PROPERTIES OF NANOCOMPOSITE FOAMS

by

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PREVIEW

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PREPARING, CHARACTERIZING, ON-LINE DIGITAL IMAGING OF RESIDENCE TIME DISTRIBUTION AND MODELING OF MECHANICAL PROPERTIES OF NANOCOMPOSITE FOAMS

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University of Nebraska, 2008

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The objectives of this research were to prepare, characterize and to study the effects of organoclay and extrusion variables on the physical, mechanical, structural, thermal and functional properties of tapioca starch (TS)/poly(lactic acid) (PLA) nanocomposite foams. On-line digital imaging processing was used to determine residence time distribution (RTD). Adaptive neuro-fuzzy inference system (ANFIS) was used to model the mechanical properties of nanocomposite foams.

Four different organoclays (Cloisite 10A, 25A, 93A, 15A) were used to produce nanocomposite foams by melt-intercalation. The properties were characterized using X-ray diffraction, scanning electron microscopy, differential scanning calorimetric, and Instron universal testing machine. The properties were influenced significantly with the addition of different organoclays. TS/PLA/Cloisite 30B nanocomposite foams, with four clay contents of 1, 3, 5, 7 wt%, were prepared by a melt-intercalation method. Among the four nanocomposites, 3 wt% clay content produced significantly different properties.

Screw speed, screw configuration, die nozzle diameter and moisture content were varied to determine their effects on organoclay intercalation. These extrusion variables had significant effects on the properties of TS/PLA /Cloisite 10A nanocomposite foams due to the intercalation of organoclay.

PREVIEW

Multiple inputs single output (MISO) models were developed to predict mechanical properties of nanocomposite foams. Four individual ANFIS models were developed. All models preformed well with R^2 values > 0.71 and had very low root mean squared errors (RMSE). Effects of screw configurations and barrel temperatures on the RTD and MISO models were developed to predict mechanical properties. The influence of the extrusion variables had a significant effect on the mean residence time (MTR).

On-line digital image processing (DIP) technique was developed to measure the RTD as compared to the colorimeter method. R^2 showed a correlation of 0.88 of a* values from both methods. The influence of screw configuration and temperature on RTD were analyzed by the MRT and variance for both methods. Mixing screws and lower temperature resulted in higher MRT and variance for both methods.

PREVIEW

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PREVIEW

THESIS FORMAT

This thesis was written as a series of six chapters suitable for publication in journals. Each chapter has its own abstract, introduction, materials and methods, results and discussion, conclusions and references.

The first chapter is an introduction, preceding the six chapters, describes the overall objective of the research. The second chapter presents the effect of types of organoclay on the properties of nanocomposite foams by melt-intercalation. The third chapter presents the effect of organoclay contents on the properties of nanocomposite foams. The fourth chapter presents the influence of extrusion variables on the properties of nanocomposite foams. The fifth chapter deals with modeling the mechanical properties as a function of input variables. The sixth chapter presents the influence of extrusion variables on the retention time distribution and models were developed using adaptive neuro-fuzzy inference system to predict mechanical properties. The seventh chapter describes the on-line digital image processing technique to measure the residence time distribution as compared to the colorimeter method. The eighth chapter, succeeding the six publication-format chapters, contains the combined recommendations for those chapters.

PREVIEW

TABLE OF CONTENTS

PREVIEW

PREVIEW

PREVIEW

PREVIEW

LIST OF TABLES

PREVIEW

PREVIEW

LIST OF FIGURES

CHAPTER II

PREVIEW

CHAPTER III

PREVIEW

CHAPTER VII

PREVIEW

CHAPTER I

INTRODUCTION

The large amount of plastics that are produced from petroleum resources, once used and discarded into the environment, ends up as nondegradable waste. For this reason, there is a need to develop biodegradable plastic materials, especially for short-term packaging that could degrade naturally.

Starch is known to be completely biodegradable in soil and water. It is inexpensive and readily available, but has severe limitations due to its solubility and poor water-resistance. Therefore it is often blended with other polymers to improve the properties. One of the most promising polymers is poly(lactic acid) (PLA) because it is produced from renewal sources. PLA is insoluble in water, has good moisture and grease resistance and good mechanical properties. However it is expensive. To reduce cost, starch is used in a higher proportion. Therefore, PLA and starch in the right combination, forms excellent packaging foams.

PREVIEW

Nanocomposite foams can be produced by melt-intercalation using an extruder. Incorporation of a small quantity of nano-sized clay particles can improve the physical, thermal and functional properties. However, these improvements are dependent upon the types and percentages of clay and on the processing conditions (screw configurations, screw speeds, temperature, etc.). The design of screw configuration and the selection of temperature and screw rotating speed are critical in the processing of nanocomposites. Sufficiently long residence time, moderate shear intensity and high extrusion temperature are known to produce nanocomposites with improved functional properties.

Residence time distribution (RTD) relates to the optimal processing conditions, and is a result of the flow patterns inside an extruder. It describes the time distribution of a material that is inside the extruder. Effects of operating conditions on RTD which affects the properties of nanocomposites have been studied. An online digital imaging processing (DIP) technique was used to analyze RTD. The resulting RTD were compared to RTD obtained by a conventional colorimeter method.

In summary, the overall objectives of this research were to:

1. Investigate the influence of types of nanoclay on the intercalation and properties of tapioca starch/PLA nanocomposite foams;
2. Investigate the influence of clay contents on the intercalation and properties of tapioca starch/PLA nanocomposite foams;
3. Investigate the influence of extrusion variables on the intercalation and properties of tapioca starch/PLA nanocomposite foams;
4. Model selected properties of the nanocomposite foams by using adaptive neuro-fuzzy inference system (ANFIS);
5. Investigate the influence of extrusion variables on RTD and modeling of the mechanical properties of nanocomposite foams using ANFIS; and
6. Determine RTD by using on-line digital imaging processing.

PREVIEW

CHAPTER II

PREPARATION AND CHARACTERIZATION OF TAPIOCA STARCH-POLY(LACTIC ACID) NANOCOMPOSITE FOAMS BY MELT INTERCALATION BASED ON CLAY TYPE

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PREVIEW

Preparation and characterization of tapioca starch-poly(lactic acid) nanocomposite foams by melt intercalation based on clay type

Abstract:

Tapioca starch (TS), poly(lactic acid) (PLA), and four different organoclays (Cloisite 10A, Cloisite 25A, Cloisite 93A and Cloisite 15A) were used to produce nanocomposite foams by melt-intercalation. Structural, thermal, physical and mechanical properties were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and an Instron universal testing machine, respectively. The first XRD peaks for all four nanocomposite foams, were observed to shift to lower angles, indicating that intercalation occurred. The extent of intercalation depended on the type of organoclay and was exhibited in the sequence of Cloisite 10A > 25A > 93A > 15A. Glass transition temperatures (T_g) and melting temperatures (T_m) of the foams were investigated by DSC. Radial expansion ratio (RER), unit density, BSI (bulk spring index), bulk compressibility, Young's modulus (E), water absorption index (WAI) and water solubility index (WSI) were influenced (p<0.05) significantly with the addition of different organoclays into the TS/PLA matrix.

Keywords: Nanocomposites; Organoclay; Properties; Extrusion; Foams

PREVIEW

1. Introduction

There is a growing interest in developing biodegradable polymers to replace synthetic nondegradable materials. Poly(lactic acid) (polylactate or polylactide) (PLA) is a biodegradable polyester that can be used to alleviate the waste disposal problem. It is synthesized from L- and D-lactic acid, which are produced from the fermentation of sugar and (poly)saccharides such as sugar feedstocks and corn, wheat and other starch sources, either by ring-opening polymerization or by condensation polymerization (Stevens, 2002). PLA is insoluble in water and has good moisture and grease resistance. Its mechanical properties can be modified by varying its molecular weight and its crystallinity. PLA is used widely as a biodegradable and renewable plastic for uses in service ware, grocery, waste-composting bags, mulch films, controlled release matrices for fertilizers, pesticides and herbicides (Fang and Hanna, 1999). However, PLA is expensive due to the complicated synthesis.

Starch is a natural polymer, inexpensive and readily available resource, and is often used as a filler for the replacement of petroleum-derived synthetic polymers to decrease environmental pollution. However, starch has severe limitations because of its solubility and poor water-resistance, making starch products very sensitive to the relative humidity at which they are stored and used (Simmons and Thomas, 1995). Starch-polyester blends are being produced with the objective of maintaining the excellent physical properties of the polyesters while reducing cost. A process was developed at the University of Nebraska-Lincoln to produce starch-based plastic foam with 70% starch combined with a variety of ingredients and plastics (Chinnaswamy and Hanna, 1993). Fang and Hanna (2000a) found that addition of PLA to regular and waxy corn starches

PREVIEW

improved the physical and mechanical properties of the foams. Recently, formation of nanocomposites with the aim to improve functional properties has become popular. One of the most promising nanocomposites is formed from organic polymer and inorganic clay minerals consisting of layered silicates.

Polymer nanocomposites are a class of reinforced polymers containing small quantities (1-5 wt%) of nanometric-sized clay particles. Smectite – type clays, such as hectorite, synthetic mica, and montmorillonite were employed as fillers to enhance the properties of the composites. The functional properties of the nanocomposites were improved markedly compared to those of the unfilled polymer or conventional composites. These improvements included high moduli (Lim and Park, 2000; Nam et al., 2001); increased tensile strength (Dennis et al., 2001) and thermal stability (Chang et al., 2003); decreased gas permeability (Yuen et al., 2006), flammability (Morgan, 2006) and water absorbance (Chiou et al., 2006); and increased biodegradability of biodegradable polymers (Ray et al., 2003).

Of the four methods (solution intercalation, in situ polymerization, melt intercalation, and template synthesis) which have been used to synthesize nanocomposites, melt intercalation is the most appealing approach because of its versatility, compatibility with polymer processing equipment, and because it is an environmentally friendly process that requires no solvent and is suitable for industrial uses (Choi et al., 2003; Li and Ha, 2003). In melt intercalation, the clay and polymer are added together above the melting temperature of the polymer; they may be held at this temperature for a period of time, put under shear, or other conditions to encourage intercalation and exfoliation of the clay (Dean and Yu, 2005).

PREVIEW

Generally, polymer/layered silicate composites are divided into three main types: tactoid, intercalated, and exfoliated nanocomposites. In a tactoid, the polymer is unable to intercalate between the silicate sheets and the properties of the composites stay in the same range as the traditional microcomposites. Intercalated nanocomposites occur when a small amount of polymer moves into the gallery spacing between the silicate platelets. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is formed (Pollet et al., 2002). The intercalated and exfoliated nanocomposites currently are of primary interest because their properties are significantly improved, even at low clay concentrations. However, the formation of intercalated or exfoliated nanocomposites depends on the type of organoclay (Choi et al., 2003; Ammala et al., 2007) the clay content (Artzi et al., 2002; Nobel and Picken, 2007) and the processing conditions (Dennis et al., 2001; Tanoue et al., 2006).

The objectives of this study were to prepare TS/PLA/clay nanocomposite foams using four different clays via melt-intercalation and to investigate the influence of the type of clay on structural, morphological, thermal, physical and mechanical properties of the foams.

PREVIEW

2. Materials and Methods

2.1. Materials

Semicrystalline poly(lactic acid) (PLA) resin of MW_n 85,000 was produced by Cargill, Inc. (Minneapolis, MN). It contained ~93% L-lactide, 2% D-lactide and 5% mesolactide. It was in the form of 2 – 4 mm spheres. The thermal properties measured by

DSC showed a glass transition temperature of 70˚C and a melting point of 174˚C. The true density of PLA resin was 1.22 g/cm ^{3}. PLA usually is used as an amorphous material in molded products because of its low rate of crystallization, though it is a semi-crystalline polymer. Commercially available tapioca starch was purchased from Starch Tech. Inc. (Golden Valley, MN). Tapioca starch was agglomerated into spherical granules of 2-4 mm diameter to facilitate feeding into the extruder. The moisture content of the tapioca starch was adjusted to 18%, dry basis, with distilled water prior to extrusion. Tapioca starch and 10% PLA (10% w/w PLA/starch) were blended with 0.5% sodium bicarbonate, 0.5% citric acid and 3% clay in a Hobart mixer (Model C-100, Horbart Corp., Troy, OH) and stored in plastic jars prior to extrusion. PLA content of 10% was selected based on preliminary experiments. Fang and Hanna (2000b) found that at 10% PLA content, the foams possessed the highest spring index and intermediate compressibility and Young's modulus values. They concluded that for practical applications, the bulk mechanical properties were more meaningful. Sodium bicarbonate and citric acid were added to degrade the biodegradable polymer into chains of between 1,000 and 100,000 Daltons or approximately 500 to 50,000 monosaccharide groups to promote expansion (Chinnaswamy and Hanna, 1993). Four commercial clays, namely Cloisite 10A, Cloisite 15A, Cloisite 25A and Cloisite 93A, were purchased from Southern Clay Products Inc (Gonzalez, TX) and used as nanofillers, hereafter referred to as 10A, 15A, 25A and 93A, respectively. They were organically-modified montmorillonite (MMT) also known as organoclays. The ammonium cations of the organoclays were dimethyl benzyl hydrogenated-tallow quaternary ammonium for the Cloisite 10A, dimethyl dihydrogenated-tallow quaternary ammonium for the Cloisite 15A, dimethyl hydrogenated-tallow 2-etylhexyl quaternary ammonium for the Cloisite 25A and

PREVIEW

methyl dehydrogenated-tallow quaternary ammonium for the Cloisite 93A. The characteristics of the clays used in this work are summarized in Table 1. Table 2 gives the five different formulations used in this research work.

2.2. Extrusion

A twin-screw extruder (Model DR-2027-K13, C. W. Brabender, Inc., S. Hackensack, NJ, USA) with corotating mixing screws (Model CTSE-V, C. W. Brabender, Inc., S. Hackensack, NJ, USA) was used to conduct extrusions. The conical screws had diameters decreasing from 43 mm to 28 mm along their length of 365 mm from the feed end to the exit end. On each screw, there was a mixing section, in which small portions of the screw flights were cut away. The mixing section enhanced the mixing action and also increased the residence time of the sample in the barrel. A 150-rev/min screw speed was used for all extrusions. The temperature at the feeding section was maintained at 50°C, the second barrel section at 120°C, the third barrel section at 150°C and die section at 170°C. A 3 mm diameter die nozzle was used to produce continuous cylindrical rope-like extrudates which were cut by a rotary cutter. The extruder was controlled by a Plasti-Corder (Type FE 2000, C. W. Brabender, Inc. S. Hackensack, NJ). Data including screw rotating speeds, barrel temperature profiles, pressure profiles and torque readings were recorded for subsequent analyses. Extrusion conditions selected were based on preliminary studies and previous experiments.

PREVIEW